POLYCYCLIC AROMATIC HYDROCARBONS IN THE CHRISTCHURCH ENVIRONMENT

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by

Lee Hian Kee

23 Tingkat Molek
Bagan Ajam
Butterworth
Province Wellesley
West Malaysia
Ph 345-808

1982

ABSTRACT

The levels of polycyclic aromatic hydrocarbons (PAH) have been determined in the Christchurch environment in the following sample types: city and suburban atmospheric particulate matter; mud in the Avon and Heathcote Rivers and their estuary; an estuarine bivalve, Chione stutchburyi, the common cockle; automobile exhaust particulates and domestic soot. More than forty PAH of four or more rings present in these samples have been identified using gas chromatography and gas chromatography-mass spectrometry. The use of [PAH]/[Pb] ratios as sensitive and discriminating source indicators for airborne PAH is demonstrated and the results strongly suggest that the domestic fire is the predominant contributor to the overall atmospheric PAH pollution in Christchurch in winter. Comparison of PAH gas chromatographic profiles and the use of parent compound distributions indicate that the major proportion of the PAH in the mud of the rivers and estuary also originates from this source. Promising preliminary studies were made on the use of ultraviolet spectroscopy as a rapid quantitative method for total PAH determination, and as a qualitative method for identifying PAH mixtures from different sources.

CONTENTS

CHAPTER 1

INTRODUCTION

1.1 CHEMICALS AND CANCER

Cancer is a generic term for a variety of diseases that affect both human beings and animals, and which are characterized by uncontrolled cellular growth. This abnormal growth is initially localized but which, if left unchecked, induces other cells to behave similarly, leading to the loss of their essential specific functions. Eventually, the tumour growth destroys surrounding tissues and afflicts other organs. All these events have deleterious effects on vital bodily functions by destroying irreplaceable organs, removing essential nutrients, and causing haemorrhages, and finally, premature death.

While there is much speculation and controversy about the nature of cancer itself, there appears to be little doubt that cancer is an environmental disease, and there have been suggestions that 70 to 90 percent of cancers are caused by environmental factors.[1-3] An example that illustrates the importance of the environment in causing human cancer is the work of Haenszel and Kurihara[4] on migrant populations. It is well known that there is a high incidence of stomach cancer in Japan whereas the converse is true in the United States. It was found[4] that the offspring of Japanese immigrants to the United States showed incidences of this type of cancer intermediate between those of the two countries. However, in second generation immigrants, the incidences were essentially the same as in the United states. These results show that the

causes of stomach cancer are probably more due to environmental than, for example, genetic factors. Nitrosamines are in fact believed to be a major cause of stomach cancer in man.[2,5]

It is generally agreed that the major causes of cancer in the environment are chemicals, and in this category of chemical carcinogens the largest known group are the polycyclic aromatic hydrocarbons (PAH).[6,7] Epidemiological studies[8] have shown that there is a higher incidence of lung cancer in urban areas compared to rural areas. An earlier study[9] which took smoking habits into account had arrived at the same conclusion. It is therefore significant that two other studies have shown that PAH levels are higher in urban than rural atmospheres[10] and lung cancer incidence is greater in areas with increased exposure to PAH.[11] These results would certainly implicate atmospheric PAH as contributors to this observed carcinogenic activity in urban atmospheres especially since they are the major class of chemical carcinogens although, of course, they are not the only pollutants present. More direct evidence of the carcinogenic potential of urban atmospheric environments has come from results of studies[12,13] on the effects on bacterial strains of organic extracts of airborne particulate matter. Specifically, it was the mutagenicity of the extracts on Salmonella typhimurium strains that was demonstrated but it is believed that there is a relationship between mutagenicity and carcinogenicity (see below).

1.2 POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAH) can be described as organic compounds containing three or more fused benzenic rings which may or may not carry alkyl groups. The structures of the better known four- to seven-ring PAH are shown in Appendix A. PAH molecules are planar and exhibit a high degree of electron delocalization. These compounds generally have low volatilities and solubilities[14] (in pure water).

The majority of PAH present in the environment are formed during the pyrolysis of carbonaceous materials at high temperatures (500 - 800°C), primarily the burning of coal and oil for heating and power generation, and of transport fuels. Refuse incineration[15] may also be included under this classification of anthropogenic PAH sources. Natural forest and grass fires[16] will contribute to the overall PAH concentration as well. A C,H-radical mechanism for the pyrolytic formation of carcinogenic PAH has been proposed by Badger and co-workers.[17-19] As an illustration, the mechanism of formation of benzo[a]pyrene by such a process is shown in Figure 1.

Another possible mode of formation of PAH is biosynthesis,[20-22] although this has been challenged;[23] at present this is an area of controversy. More recent results,[24] however, appear to indicate that it is bioaccumulation rather than endogenous formation that is responsible for the presence of PAH in plants and bacteria. Nevertheless, some PAH apparently are generated by biotransformations of biogenic precursors. A well-documented example is perylene found in sediments.[16,25-28]

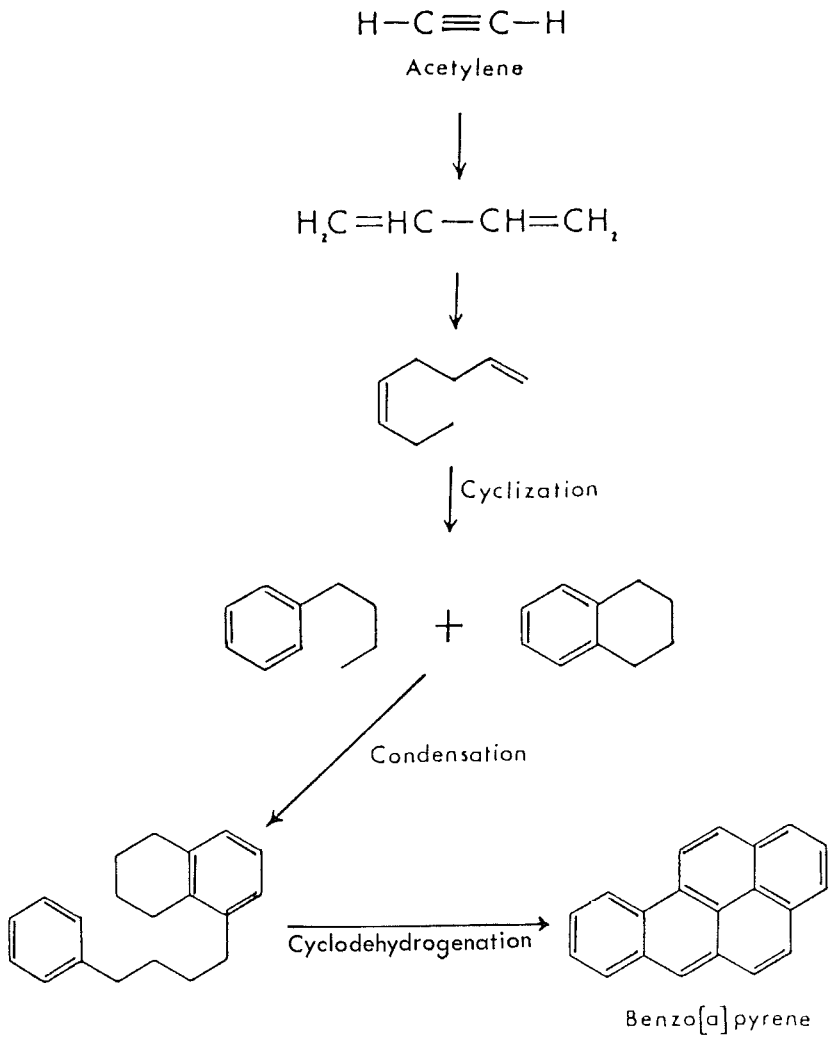


Figure 1. Mechanism of pyrolytic formation of benzo[a]pyrene as proposed by Badger and Novotny.[17]

With the predominant mode of formation of PAH being incomplete combustion of organic material, most of these compounds are adsorbed on airborne particulate matter (soot and fly ash) formed in the combustion process.[29] When the various modes of transmission of airborne particulates in the environment are considered (e.g. wind, precipitation, the water cycle and food web), it is not difficult to

understand the ubiquity of PAH in the world. Although there are certain exceptions, most of the larger PAH are relatively stable chemically; this may explain their persistence in the environment.

1.2.1 Polycyclic aromatic hydrocarbons as carcinogens

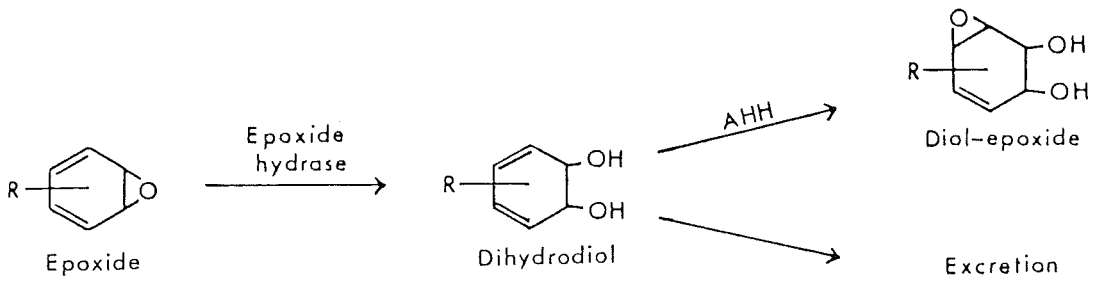
PAH have been the subject of extensive investigations on chemical carcinogenesis since 1774, although the existence of such compounds was then unknown. Resulting from this early study was the link between scrotal cancer which afflicted chimney sweeps and the contact of the victims with soot. Further studies on the unknown chemicals derived from coal tars led initially to the finding that the carcinogenic compounds were PAH, and then to the isolation of the first chemical carcinogen, benzo[a]pyrene, from gas works pitch.[30] Benzo[a]pyrene remains one of the most potent carcinogenic PAH known today.

Laboratory tests[14] have shown that several other PAH are carcinogenic in animals and while there is a need for caution when extrapolating these results to man, these compounds, including benzo[a]pyrene, are suspected to be causes of human cancer as well. In studies on the carcinogenic properties of PAH, much work has been done to ascertain just how compounds such as these become activated and subsequently induce cancer in an organism.

In vivo and *in vitro* studies indicate that PAH are metabolized to various derivatives, which in an organism, would be suitable for excretion. Ironically, it is this

natural detoxifying system that leads to an increased risk of cancer. The metabolites resulting from these processes are believed to be the carcinogenic agents that induce the transformation of normal cells into cancerous ones.

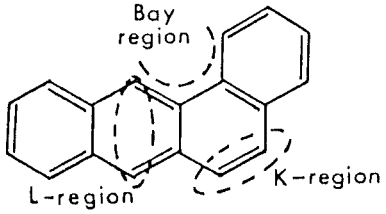
The two most well-known proposals for the identity of this active metabolite are the epoxide and the diol-epoxide of the PAH. The epoxide is formed by the action of an enzyme, aryl hydrocarbon hydroxylase (AHH) during the detoxification process, and then converted by epoxide hydrase to a dihydrodiol which may conjugate with glucuronic acid and be excreted. It is also possible for the dihydrodiol to react again in conjunction with AHH to give a diol-epoxide.



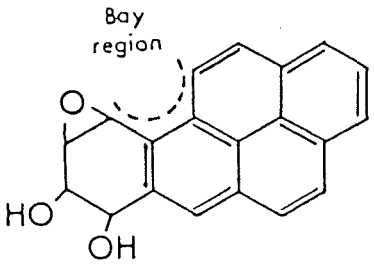
Whichever of these two metabolites is the ultimate carcinogen is a matter of contention (but see below), but it is believed to bind with cellular macromolecules like deoxyribonucleic acid (DNA), ribonucleic acid (RNA) or protein (all of which are nucleophilic in character). Most investigators agree that DNA is the target for this active metabolite. The intercalation of the epoxide or diol-epoxide into the DNA strand results in possible frameshift errors in

subsequent DNA replication. This is thought to be the first step towards the formation of cancer. Strictly speaking, an error in the DNA sequence causes a mutation, and while it has been stated[31] that all ultimate carcinogens are also mutagens, there is no conclusive proof as yet. The parallelism is generally accepted, however. It is thus possible that PAH are carcinogenic because of the mutagenic properties of their metabolites. Induction of cancer by mutations of the DNA strand may seem like an oversimplified view, but there is a positive correlation between carcinogenic activity and the extent of binding of PAH metabolites.[32] Moreover, there is no threshold dose for cancer induction; carcinogenic effects are produced by extremely small doses of PAH in laboratory animals,[33] unlike other toxic chemicals which act within the cell in different ways, and possess definable threshold levels. Initiation of tumorigenesis requires DNA synthesis implying that the causative agents are acting on the DNA and by altering genetic activity, are causing cancer.

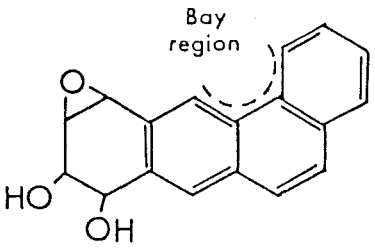
Attention has also been directed towards the possible relationship between the chemical reactivity of a specific bond in a PAH and its carcinogenic activity. Pullman[34] originally introduced the term K-region to describe the bond with the greatest double bond character in a PAH.



Benz [a] anthracene



A



B

For many compounds, high pi electron density appeared to be related to carcinogenic activity; this seemed to indicate that the interaction between the PAH and the cell took the form of an addition reaction at the K-region, and this initiated the cancer. In some PAH however, the presence of another reactive region (L-region)[35] could override the addition at the K-region. Thus, addition at the K-region occurred only if the L-region was less reactive or absent.

K-region epoxides were then thought to be the ultimate carcinogen but a new hypothesis[32] came to the fore when non K-region diol-epoxides of benzo[a]pyrene (A) and benz[a]anthracene (B) were discovered to bind the DNA in vivo. The epoxide and diol functional groups of both PAH are on the angular saturated benzo-ring forming the bay region.[36]

These results suggest that the diol formed from the metabolism of the epoxide may be an intermediate in the binding of these PAH to DNA. A possible general mechanism of the metabolic activation of PAH[32] appears to be that the

non K-region diol is initially formed and is subsequently converted to a diol-epoxide. The latter, which somehow resists further metabolism, then reacts with the cellular DNA.

The development of the bay region (diol-epoxide) theory has apparently shifted interest away from the K- (and L-) region (epoxide) theory although it has been suggested[37] that the reactivity of the bay region is to a certain extent affected by that of the L-region. All in all, the situation is still very inconclusive. Nevertheless, what emerges from all these studies is that there is now no doubt about the carcinogenicity of many PAH found in the environment (see Appendix A).

1.2.2 Determination of polycyclic aromatic hydrocarbons

Whether in the air, water, soil or food, PAH are present as extremely complex mixtures. This is not surprising since they are formed from hydrocarbons which, apart from their enormous structural variety, also originate from a great diversity of sources. Moreover, the nature and variability of combustion processes inevitably result in a range of products of varying compositions.[38]

The carcinogenic properties of PAH, coupled with their widespread presence and persistence, pose a great risk to the health of the human population, which in turn provides the essential reason for the need for environmental PAH determination. With the increasing use of fossil fuels and the rapid rate of industrialization (as more developing nations

are committing themselves to urbanization and industrialization programmes), the occurrence of PAH in the environment should be of concern to health authorities.

An important aspect of PAH determination is the requirement for qualitative and quantitative information about individual components, for the following reasons:

(a) The carcinogenicity of individual PAH varies widely (see Appendix A). Even isomeric ring and alkyl-substituted systems differ considerably in biological activity (presumably due to the facility or otherwise with which they interact with cellular DNA). For example, benzo[a]pyrene is one of the most potent carcinogens known but benzo[e]pyrene is only slightly carcinogenic,[30] if at all[32,39] (although it is co-carcinogenic in the presence of benzo[a]pyrene[39]); 1- to 4- and 6-methylchrysenes are all only marginally carcinogenic compared to the strongly active 5- isomer.[40] To establish the danger that environmental PAH represent, it is therefore necessary to identify and quantify individual compounds in a complex mixture.

(b) As already described, different PAH assemblages are produced under varying (high) temperatures from organic material derived from different sources. Thus, if PAH components can be identified and quantified individually, then perhaps the ability to describe the sources and fates of these compounds may be improved. In remote places, away from human activities, details about the identities and quantities of individual PAH may enable the identification of possible non-anthropogenic sources of some of these compounds although, as has been pointed out above, the likelihood of PAH originating from such sources is still at issue.

1.2.3 Analytical techniques for PAH determination

Not only are PAH mixtures extremely complex in environmental samples, they usually form only a portion of the total organics (and other materials) present in a particular sample. Taking these factors into consideration, it is usually advantageous to include three main features in any analytical technique for PAH. Firstly after collection, the sample is extracted for its total organic (i.e. including PAH) content. Secondly, the PAH are isolated from the rest of the organic content as well as other materials, if present. Finally, the separation of the PAH mixture into individual components is carried out prior to (or during) identification and quantification. It is also sometimes useful before the third stage to fractionate the PAH mixture by ring numbers, using chromatographic methods, to simplify the final analysis.

Different solvents and solvent-mixtures have been used for PAH extraction from the sample matrix, a procedure usually performed with a Soxhlet apparatus, or by ultrasonification or vacuum sublimation.[41] In the case of biological samples, the tissues are usually homogenized, then saponified under reflux. Liquid-liquid extractions and (usually column) chromatographic techniques have been the most commonly used methods for the isolation of PAH from the organic and other extraneous materials. A variety of solvent systems have also been used for liquid-liquid partitions. An alternative to the latter is pre-concentration on synthetic resins[42] from which subsequent removal of the PAH adsorbed is achieved by solvent-stripping or by thermal desorption.

Gas chromatography (GC), high performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) have all been used for separating PAH components.[41] The identification of components can be accomplished by comparison of retention times of available reference compounds (GC and HPLC) and photodetection (column chromatography, TLC, HPLC and more recently, GC). Quantification is achieved by the use of internal standards and/or by photometric techniques. For enhanced specificity, it has become almost standard practice to use some of these chromatographic techniques in conjunction with specific detectors such as spectrophotometers and mass spectrometers.

The combination of a gas chromatograph with a mass spectrometer provides for a detection and identification system which is more sensitive than either of the techniques individually. The mass spectra of individual peaks which are recorded during elution from the gas chromatograph, together with retention time data, normally enable many of the PAH present in a complex mixture to be identified in as little as nanogram amounts. The feasibility of using capillary columns (themselves a very significant advance on packed-column GC) in a gas chromatography-mass spectrometric system for PAH determination has been well demonstrated for a host of environemtal samples.[6,27,38,43-50] The vast improvement in resolution and sensitivity has meant that this is probably the method of choice[7,51] for this type of analysis although the comment has been made[41] that it may be too specialized for routine analysis. Apart from the more

common electron impact mass spectrometric studies, the use of other ionization techniques has been introduced in recent years.[42] These include chemical ionization (CI), field ionization, field desorption and photoionization. CI has been used [52,53] mainly to try and differentiate between mass spectra of PAH of identical molecular masses which are usually indistinguishable by electron impact ionization mass spectrometry, whereas the other methods are used principally to obtain almost "clean" molecular-ion spectra for the determination of molecular mass distributions of mixtures.[42]

Mass spectrometry on its own has also been used for the analysis of complex mixtures. A high-resolution mass spectrometric technique in which identification and quantification of atmospheric pollutants including individual PAH was handled by computer, has been described.[54] A relatively new technique is that of metastable ion mass spectrometry,[55] in which daughter-ion spectra resulting from the fragmentation of pre-selected molecular (parent) ions were used to distinguish between PAH of identical molecular masses (chrysene, benz[a]anthracene, triphenylene and naphthalene were used in this example).

Of the spectroscopic detection methods, ultraviolet (UV) absorption has been the most widely used,[41] initially with fixed wavelength, subsequently with variable-wavelength detectors. Normally, UV detection is used with the various chromatographic methods.[56-65] Combined with high performance liquid chromatography, fluorimetric detection is becoming a popular technique for PAH determination,[66-68] being more

sensitive and specific than UV absorption methods[41,69] (and additionally, extensive sample clean-up is avoided[66]).

Also giving higher sensitivity and specificity than absorption methods are phophorescence techniques,[42,69] useful when a mixture contains strongly fluorescent but weakly phosphorescent interfering components. Two components with interfering fluorescence can therefore be separated by their phosphorimetric measurements.

Nuclear magnetic resonance (NMR) spectroscopy has its value in the identification of alkyl-substituted isomers of PAH, a problem not normally solved by the use of methods like mass spectrometry or sometimes, GC, especially if reference compounds are lacking. For example, conventional ^{1}H NMR has been used to identify methyl-substituted pyrenes in mixtures.[70] The advent of rapid spectral accumulation through Fourier-transform techniques has enabled even smaller PAH samples (less than 1 mg) to be analysed by NMR. Thus, it has been possible to identify methylchrysene isomers in a PAH mixture extracted from atmospheric particulates, and from tobacco and marijuana smoke condensates.[44a,71]

A technique used mainly to resolve PAH isomeric mixtures is infrared spectroscopy, which, like NMR spectroscopy, has been aided by the introduction of matrix-isolation Fourier-transform data gathering procedures. Several investigations of this method have been reported;[72,73] a recent addition to this line of PAH studies is one in which a gas chromatograph fitted with a capillary column was interfaced to an infrared detector.[74]

Because no single technique is considered fully adequate for PAH determination, there have been a few attempts to devise integrated schemes comprising several techniques. Thus, the combination of gas chromatography - mass spectrometry (GC-MS), HPLC and NMR spectroscopy has been used.[44,71,75] More recently, an integrated approach involving GC-MS, liquid chromatography (LC) and UV spectroscopy has been described.[76] The LC-UV combination was used to provide isomer-specific identifications of PAH.

1.3 THIS WORK

Historically, the city of Christchurch (population approx. 300 000[77]) has had an air pollution problem, especially during winter when the combination of climatic and topographical conditions often lead to a stagnant layer of cold air which envelops the city. Under such conditions, the levels of pollutants in the atmosphere can attain high levels since the dispersal of pollution is inhibited by the stable inversion layer. Christchurch is on the whole lightly industrialized and there are approx. 158 000 motor vehicles in the city.[78] During winter a popular form of heating is domestic fires.

This thesis describes the study of PAH in the Christchurch environment during winter. The emphasis is on atmospheric PAH (i.e. PAH adsorbed on airborne particulate matter). The principal objective was to identify and measure the concentration of these compounds. PAH concentrations were obtained from several sites representative of various PAH sources,

and quantitative relationships between individual components as well as between total PAH concentrations and those of another atmospheric pollutant, lead, were statistically analysed to see whether these correlations could be used as a means of identifying the PAH sources. Car park building and automobile exhaust particulate matter, and domestic soot samples (all known PAH sources) were also analysed to provide reference data for the two likely major sources of atmospheric PAH. The application of the total PAH : total lead relationship to various city air pollution samples was also undertaken.

Glass capillary GC was used for quantification, and both GC and GC-MS were used for qualitative analysis.

The Christchurch urban area is drained by the Avon and Heathcote Rivers both of which flow into a common estuary. Mud along various points of the rivers and from the estuary was sampled and analysed for its PAH content. Results were examined to determine the possible sources of these PAH. Tissues of a marine bivalve, Chione stutchburyi (the common cockle) found in the estuary were also extracted and analysed. An explanation is offered for the observed distribution of total PAH along the rivers and the estuary, as well as for the levels obtained in Chione in relation to the surrounding mud and areas of the estuary from which specimens were collected.

The possibility of developing a quick and reliable method of total PAH determination was considered and led to a preliminary study of the ultraviolet (UV) absorption

characteristics of PAH mixtures. Arising from this, the feasibility of using the qualitative differences in UV absorption profiles of PAH mixtures to determine the sources of PAH was explored.

CHAPTER 2

RESULTS AND DISCUSSION

2.1 ANALYTICAL CONSIDERATIONS

2.1.1 Problems with contamination

A feature of any trace analysis, and PAH determination in particular, is the problem of contamination. As mentioned previously, an environmental sample contains many organic and other compounds. The extraction procedure used to separate the PAH from these other compounds is complex and uses large volumes of solvents, and there is much sample handling and transfers involved - all these could lead to far greater contamination than the total PAH concentration being measured. Thus, to ease the burden on the analytical procedure, contamination should be kept to a minimum, if not eliminated altogether. Because of the ubiquity of PAH in the environment, contamination by extraneous PAH is always a possibility, and it is essential to ensure that this does not occur. To this end, the purity of all the solvents (Analytical- and Reagent-grade) used in this work was checked before they were used. The solvents were concentrated down to ca. 0.5 mL from the total volumes required for an extraction, using a rotary-evaporator. The concentrates were then analysed by gas chromatography (GC). All were found to contain significant quantities of impurities which would have interfered with the PAH determination. Pre-treatment of all solvents before they were used was therefore carried out. Methods of solvent

purification are described in the Experimental Section. Also described is the treatment of filters and thimbles - the other possible causes of contamination - prior to use.

A single rotary-evaporator was used throughout this work. The vacuum-release inlet of the evaporator was fitted with a filter monitor, identical to that used for sampling, so that airborne dust was prevented from being drawn by suction into the equipment during vacuum release. As an added precaution, a second monitor was installed at the outlet leading to the water pump. A further precaution was that all extractions and sample processing was carried out in a room set aside for the purpose.

2.1.2 Cyclohexane as solvent

Cyclohexane, acetone and benzene have been shown to be equally efficient in the extraction of benzo[a]pyrene,[79] as has benzene-methanol,[80] for PAH in general. Cyclohexane, however, was chosen for the Soxhlet extraction because it is more selective - it extracts fewer extraneous materials than the other three solvents.[60,66,80,81] (The selectivity of cyclohexane compared to benzene was confirmed in this study.) Moreover, benzene is toxic and acetone is difficult to purify.[82]

2.1.3 Blank extractions

To determine the level of possible extraneous and adventitious contamination resulting from normal sample clean-up, an 8-h Soxhlet extraction was carried out with

cyclohexane only (80 - 120 mL) and the "extract" taken through the entire analytical procedure. No measurable interferences were observed in the gas chromatographic traces.

Earlier blank extractions had resulted in unacceptable contamination levels which were eventually traced to the normal laboratory supply of distilled water. All subsequent work was therefore carried out with water distilled from an all-glass still.

2.1.4 Internal standard

Benzo[b]chrysene was used as the internal standard for PAH quantification by GC. This internal standard method is based on the principle that a known weight of benzo[b]chrysene, added at the beginning of the Soxhlet extraction, would be subjected to the same analytical treatment as the other PAH in the sample. By comparing their peak areas with that of benzo[b]chrysene, PAH losses during such sample treatment are thus corrected for. Quantitative measurements made from the peak area ratios should therefore give the actual concentration of each component in the original sample. Extractions of genuine samples showed no trace of benzo[b]chrysene, justifying the use of this PAH as the standard. Blank extractions, in which benzo[b]chrysene was taken through the entire extraction scheme (including the Soxhlet operation), showed a recovery rate better than 90 percent.

2.1.5 Hydrolysis of bivalve tissue

It has been stated[83] that extraction of PAH from insoluble biological samples with boiling methanol is inefficient because these compounds are strongly adsorbed on the tissues which are not sufficiently destroyed by the hot methanol. The quantitative extraction of PAH from such samples therefore has to be carried out by hydrolysis. For marine samples, both sodium hydroxide[84,85] and potassium hydroxide[69,86-89] have been used for saponifying the tissue before solvent extraction. In this work, 2 M potassium hydroxide in aqueous methanol was used for the bivalve samples. Hydrolysis has to be complete, to avoid the formation of emulsions during subsequent liquid-liquid extractions. (Experimental Section 3.3.1b), and some time was spent in optimising the hydrolysis conditions to give extractions free from emulsions.

2.1.6 Airborne particulate matter (APM): sampling sites

The sites for collecting APM were chosen to represent a broad range of possible pollution sources based on empirical considerations. Because of climatic conditions, especially prevailing winds, pollution from sources representative of a particular region obviously cannot be strictly confined within that area. Nevertheless, a broad generalization can be made of the main types of pollution in Christchurch and the areas most affected by them. The sites were located at Bealey Avenue, Manchester Street and Avonside (see Figure 2), and the Woolston industrial area (Figure 15, Section 2.4).

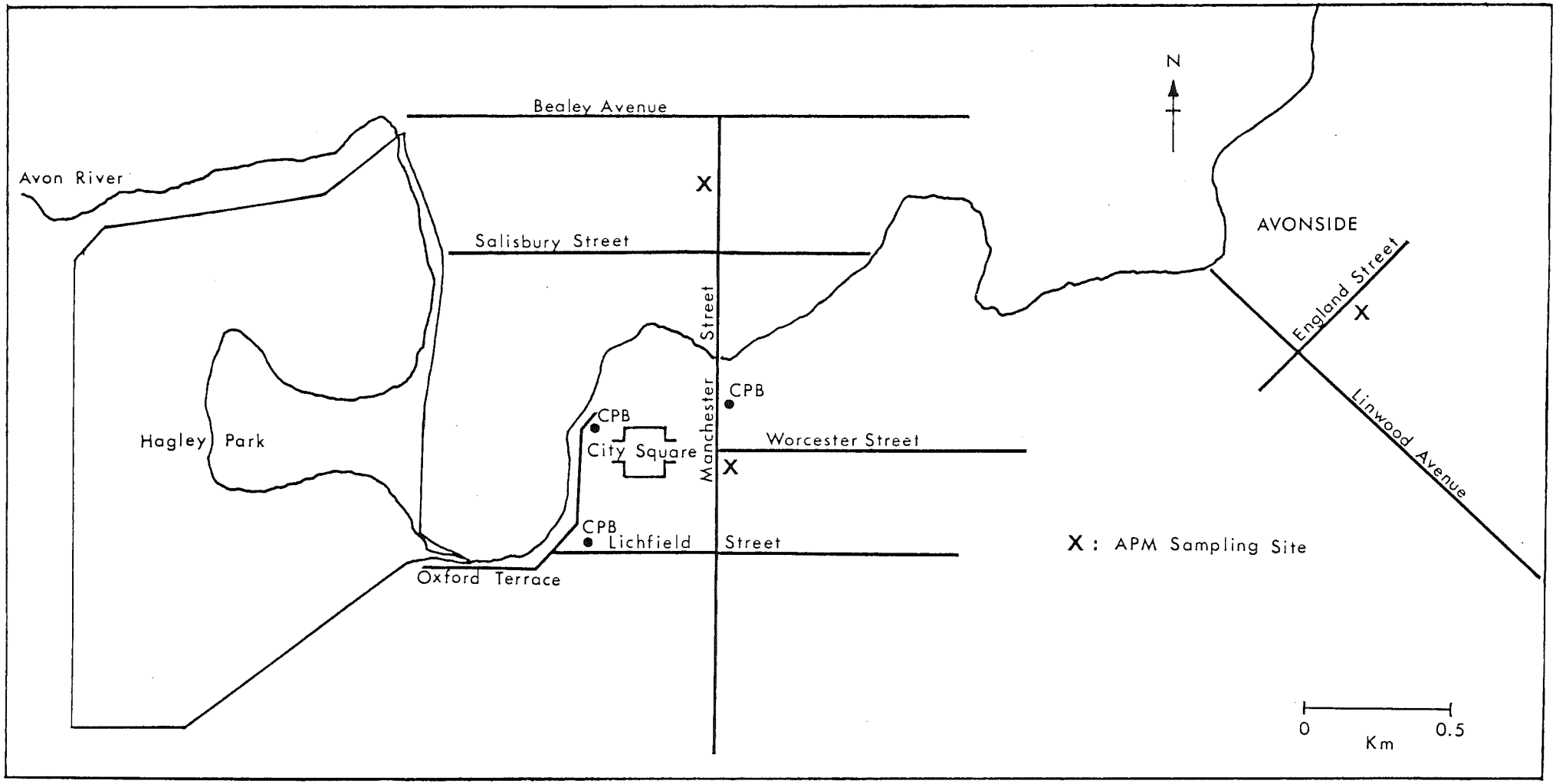


Figure 2. Map showing APM sampling sites (X) at Manchester Street, Bealey Avenue and Avonside. Car park building (CPB) locations are also shown. The Woolston site is in the Woolston industrial area (see Figure 15, Section 2.4).

The pollution at Avonside (residential suburb) should be dominated by domestic sources whereas Bealey Avenue (mainly residential on the side away from the city centre) should be intermediate between traffic and domestic domination. Manchester Street (city) should be strongly traffic-dominated and Woolston should be affected by industrial pollution to a certain extent.

2.1.7 Sephadex LH-20 chromatography

The procedure of sample extraction and clean-up used in this work is fully described in the Experimental Section but one aspect of it is elaborated here. This is the size-exclusion chromatography using Sephadex LH-20, a lipophilic gel through which elution of PAH by the eluting solvent 2-propanol is in the order of increasing ring-size. Only the fraction containing PAH of four or more rings was collected for the following reasons: (i) PAH of three rings or less are not as stable as those of four rings and above (see below); (ii) a faster gas chromatographic analysis can be achieved because a relatively high column temperature can be used in the absence of the low molecular mass components, and (iii) the carcinogenic PAH all have four or more rings.[32] (Fluoranthene and pyrene - both 4-ring PAH - do not have tumour-producing properties although they are co-carcinogenic when combined with the carcinogenic benzo[a]pyrene.[39])

Elution volumes generally tend to change slightly over a period of time due to the settling down of the column packing; accordingly, these were checked periodically for the Sephadex LH-20 chromatography.

2.1.8 Gas chromatographic analysis

The lack of pure reference compounds has always been a major problem in the identification of PAH in environmental samples by gas chromatography (GC). Capillary column GC is an excellent technique for separating complex mixtures but less satisfactory for identification, if reference compounds are unavailable. For this work, only the following pure PAH were available: fluoranthene, pyrene, benz[a]anthracene, 4-methylchrysene, benzo[j]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[b]-chrysene, benzo[ghi]perylene, anthanthrene, coronene and picene (see Appendix A). Fortunately, as will be seen later, these PAH represent the major components of all the Christchurch samples analysed (irrespective of the sources).

All the major peaks in the chromatograms were identified by comparison of their retention times with those of the reference compounds. Relative retention time data from literature sources[44b,83,90-92] also provided a useful guide to the identification of these major peaks, as well as the minor components. A third contribution to the identification exercise was the use of "doped" samples. This involved the addition of one known PAH (or more than one, provided they can be distinguished on the chromatogram) to a previously analysed sample which was then re-chromatographed. The increase in concentration (measured by peak area or height) of a particular component relative to the other peaks in the second chromatogram when compared to the original concentration as shown by the first trace would therefore establish

the identity of that component. This method is again hindered by the lack of pure reference compounds. Its other limitation is that some isomers (ring and alkylated) may have identical retention times - this could lead to peaks being assigned incorrect identities.

2.1.9 Gas chromatography - mass spectrometric analysis

As stated above, the advent of capillary columns has brought about a tremendous increase in the resolving power of gas chromatographic systems, and when coupled to the mass spectrometer the combination becomes the most powerful tool for PAH determination available today. When the lack of pure reference standards diminishes the usefulness of capillary column GC as an identification technique, the role played by the mass spectrometer assumes even greater importance. It is essential that a mixture of PAH of identical molecular masses be adequately separated by the gas chromatographic system before mass spectral analysis. This is because under electron impact conditions, the mass spectra of these isomeric PAH are almost identical. Thus, if a single peak on a gas chromatographic trace consists of two or more unresolved isomers, its mass spectrum will give no indication of the number or identity of these components. The high separating capability of capillary column GC is therefore a pre-condition for the acquisition of high quality mass spectra for the unambiguous characterization of individual components.

The electron impact mass spectra of PAH consist mainly of a very intense molecular ion which is generally the base

peak. Also present are peaks of lower intensity due to the loss of one to four hydrogen atoms. The $(M+1)^+$ molecular ion is always observed and is due to the ^{13}C isotope. The unsubstituted PAH undergo hydrogen cleavage of the molecular ion giving $(M-2)^+ > (M-1)^+$ in intensity. Quite common are the doubly charged ions $M^+/2z$ and $(M-26)^+/2z$ which are usually about 20 percent of the abundance of the molecular ion.[42]

Monomethylated PAH generally show the molecular ion as the base peak, followed by $(M-1)^+ > (M-2)^+ > (M-3)^+$. The intensity of the $(M-1)^+$ ion is often enhanced if the methyl group is located at such a position that ring closure to a five- or six-membered ring occurs with loss of a hydrogen atom from the methyl group. This arrangement gives rise to a pi electron system which stabilizes the positive charge of the resulting ion. For other alkylated PAH, the ion series, $(M-15)^+$, $(M-29)^+$, ... is observed. In methyl-substituted compounds the $(M-15)^+$ ion is not as prominent because of the favourable loss of a proton resulting in the formation of ions analogous to the tropylium ion. This is, of course, not unexpected in view of the favoured formation of the $(M-1)^+$ ion from a methylated PAH mentioned earlier.

PAH carrying methylene bridges (e.g. fluorene) also exhibit the molecular ion as the base peak, followed by $(M-1)^+$, $(M-2)^+$, $(M-3)^+$ and $(M-4)^+$ due to hydrogen cleavage. The intensity of the $(M-1)^+$ ion is often higher than that of monomethyl derivatives.

2.1.10 Discussion of errors

An analytical method of the nature considered in this work is subject to random and systematic errors as well as sampling errors. Preliminary studies indicated that the PAH levels for a particular sample could be determined by GC within ± 5 percent precision for the larger peaks and ± 10 percent for the smaller peaks. The accuracy of the method was tested with standard mixtures of PAH and authentic samples, and the reproducibility of the quantitative method was periodically checked by analysing separate but equivalent samples, and also a particular sample more than once. Overall, all PAH determinations were considered to be reliable to within ±10 - 15 percent.

The high recovery rate of more than 90 percent for benzo[b]chrysene, the internal standard, has already been discussed above; the recovery rates for the other PAH have all been shown to be better than 70 percent[83,93,94] for this method of analysis.

For the lead determinations, reliability of measurements was within ± 5 - 10 percent for all samples.

2.2 PAH IN THE CHRISTCHURCH ENVIRONMENT

2.2.1 Identification of PAH by gas chromatography and gas chromatography-mass spectrometry

More than forty PAH of four to seven rings have been identified in this work in the Christchurch environment (as well as in automobile emissions) using gas chromatography (GC)

and combined gas chromatography-mass spectrometry (GC-MS) (Table I). About a third of these components were positively identified by the gas chromatographic techniques described above; confirmatory evidence of their identities was provided by GC-MS. These major peaks (see Section 2.1.8) appear in all samples, regardless of their sources, and form a substantial proportion (ranging from 45-90 percent, depending on the type of sample) of the total PAH concentration of each sample. Glass capillary column (OV-101-coated) gas chromatograms of PAH in various samples are shown in Figures 3-8. Peak numbers referred to in the following discussion correspond to those shown in Table I and Figures 3-8.

Satisfactory resolution of the critical pairs of ring isomers benz[a]anthracene/chrysene and benzo[a]pyrene/benzo[e]pyrene was achieved using the capillary column. It is essential to separate the individual members of the two pairs of isomers because only one of each pair (benz[a]anthracene and benzo[a]pyrene) is carcinogenic - if the carcinogenic potential of a complex environmental PAH mixture is to be evaluated then it is imperative to have information on the relative concentrations of the carcinogenic and non-carcinogenic isomers in the sample. Separation between the members of these two isomer-pairs could be improved but was sacrificed in favour of a faster analysis time. A comparatively high column temperature, under both programming and isothermal conditions (see Experimental Section), for the gas chromatographic analysis

Table I. List of PAH Identified in the Christchurch Environment (and Automobile Exhaust Emissions) by Gas Chromatography and Gas Chromatography - Mass Spectrometry

Peak No.	Mr(amu)	PAH	Abbreviation
1	228	Benz[a]anthracene/cyclopenta[cd]pyrene	BaA/CYC
2	228	Chrysene	Chr
3	252	Benzofluoranthenes ([b],[j] + [k] isomers)	BF
4	252	Benzo[e]pyrene	BeP
5	252	Benzo[a]pyrene	BaP
6	252	Perylene	Pe
7	266	Methylbenzofluoranthene/methylbenzopyrene	
8	266	Methylbenzofluoranthene/methylbenzopyrene	MeBF,MeBP
9	266	Methylbenzofluoranthene/methylbenzopyrene	
10	264	Methylenebenzo[e]pyrene	MethBeP
11	264	Methylenebenzo[a]pyrene	MethBaP
12	278	Dibenz[a,j]anthracene	DBajA
13	276	Indeno[1,2,3-cd]pyrene	IP
13a	278	Dibenz[a,c]anthracene + dibenz[a,h]anthracene	
13b	278	Picene	
14	276	Benzo[ghi]perylene	BPe
15	276	Anthanthrene	An
16	290	Methylbenzo[ghi]perylene, other methyl derivatives of PAH of Mr 276	MeBPe,etc.
17	292	Methyldibenzanthracene	
18	292	Methyldibenzanthracene	MeDBA
19	292	Methyldibenzanthracene	
20	292	Methyldibenzanthracene	
21	302	Dibenzofluoranthene	DBF
22	302	Dibenzofluoranthene	
23	302	Dibenzofluoranthene	DBF,
	300	Cyclopentabenzo[ghi]perylene	CBPe
24	300	Cyclopenta[ef]benzo[ghi]perylene	CBPe
25	300	Cyclopenta[bc]benzo[ghi]perylene	
26	300	Coronene	Co
27	302	Dibenzopyrene*	DBP
28	302	Dibenzopyrene*	
29	202	Fluoranthene	

Table I Continued

Peak No.	Mr (amu)	PAH
29a	202	Benzacenaphthylene
	218	Ethylcyclopenta[def]phenanthrene
30	202	Pyrene
31	216	Benzofluorenes + methylpyrenes/methylfluoranthenes
32	228	Benzo[c]phenanthrene
		(+ Mr 234: benzo[b]naphtho[2,1-d]thiophene)
33	226	Benzo[ghi]fluoranthene
34	226	Unknown
35	234	Benzonaphthothiophene
36	242	Methylbenzo[c]phenanthrene
37	242	Methylchrysene/methylbenz[a]anthracene
38	242	Methylchrysene/methylbenz[a]anthracene
39	240	Dibenzo[def,i]fluorene or 4-H-cyclopenta[def]chrysene
40	240	4-H-cyclopenta[def]triphenylene or 4-H-benzo[fg]pyrene
		(+ Mr 254: binaphthyl)
41	256	Ethylchrysenes + ethylbenz[a]anthracene
42	268	Methylbinaphthyl
43	276	Dibenzo[b,ghi]fluoranthene, dibenzo[b,mno]fluoranthene, dibenzo[a,ghi]fluoranthene, indeno[1,2,3-cd]fluoranthene, cyclopenta[cd]perylene, acenaphth[1,2-a]acenaphthylene + phenanthro[10,1,2,3-cdef]fluorene
	278	Dibenz[a,i]anthracene + pentacene

* See Appendix A for examples of dibenzopyrenes

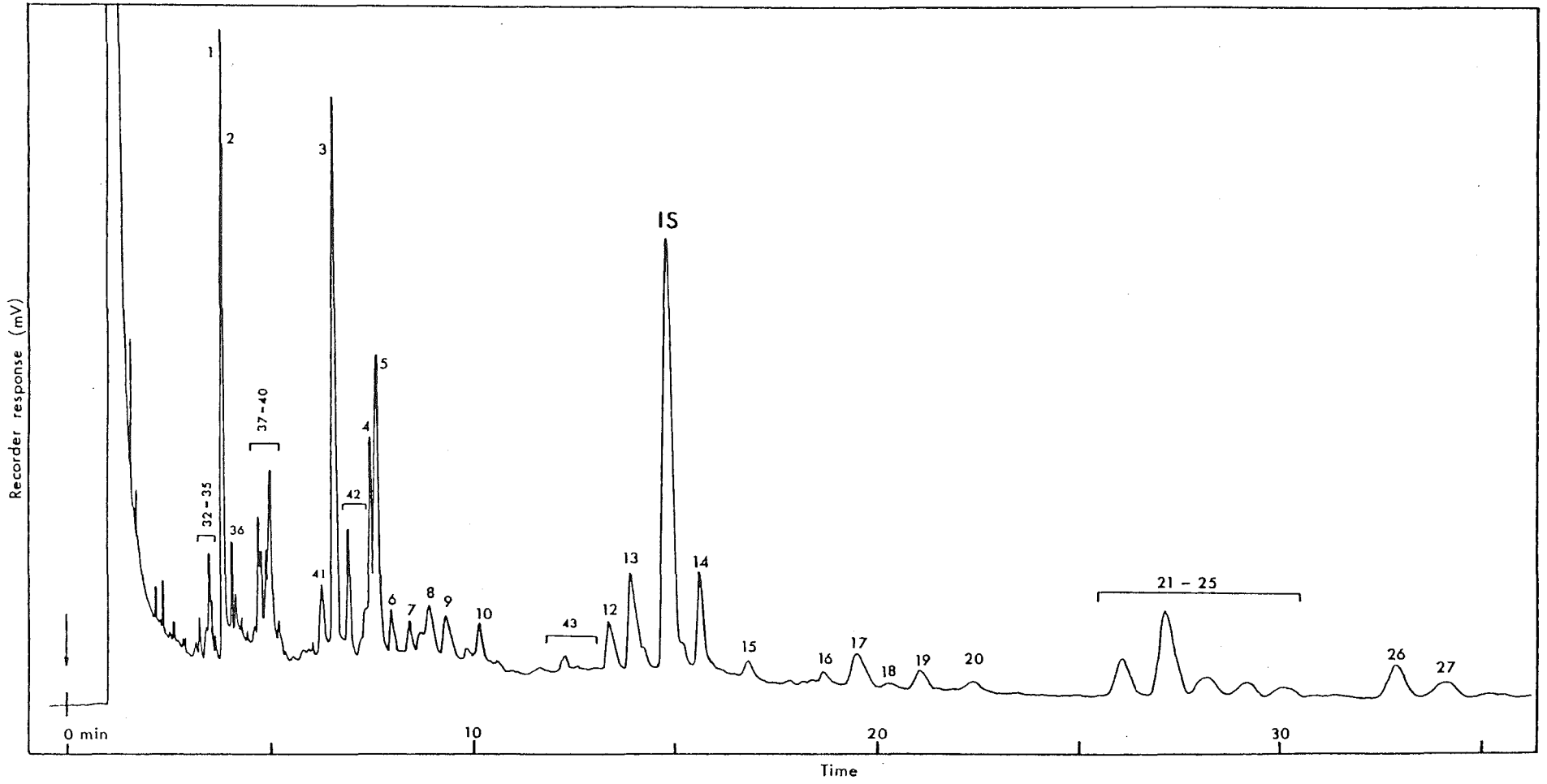


Figure 3. Gas chromatogram of PAH in Avonside APM. Column temp. 260°C, isothermal (see Experimental Section for details). Peak identities are given in Table I. IS = internal standard (benzo[b]chrysene).

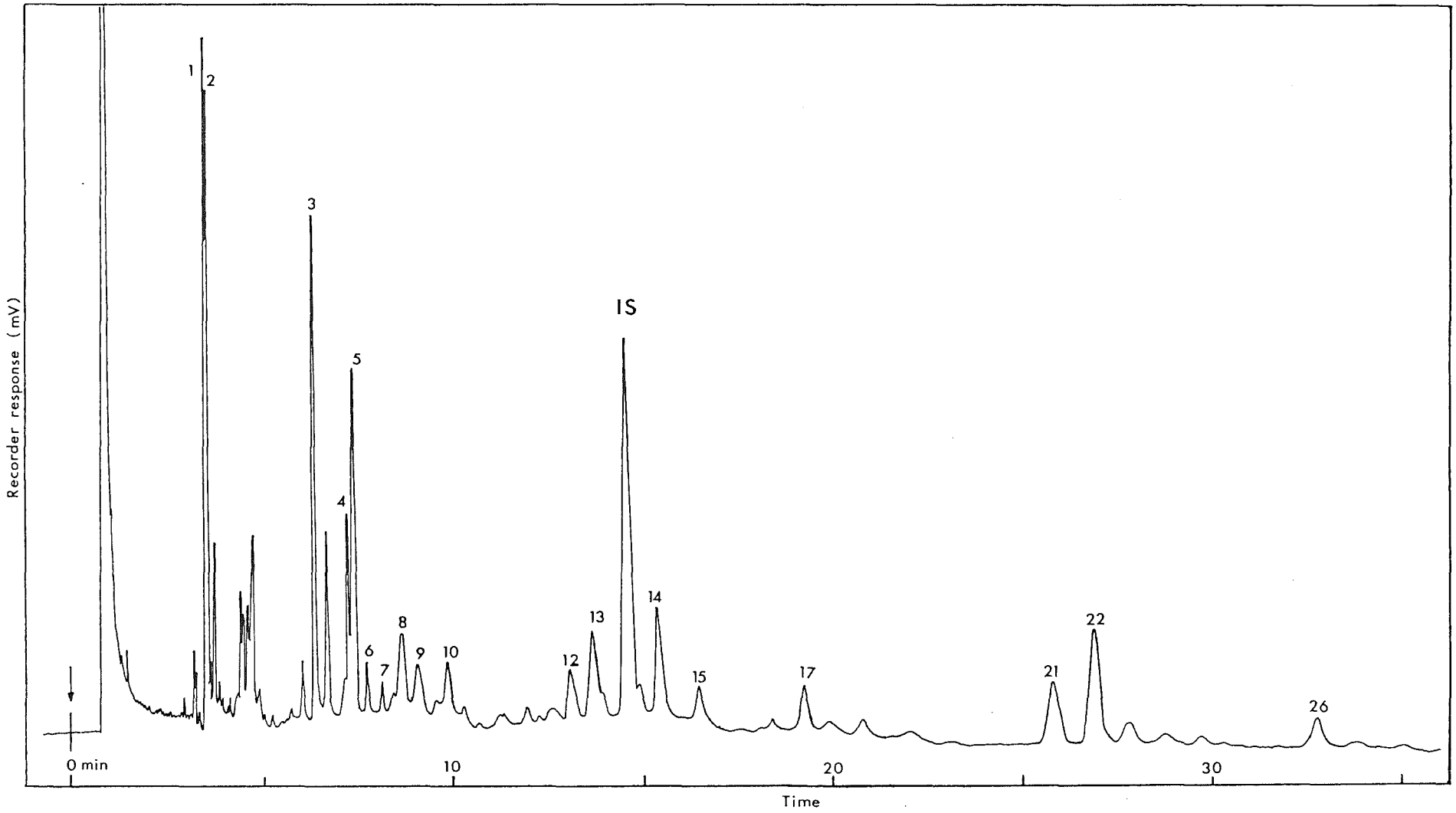


Figure 4. Gas chromatogram of PAH in Manchester Street APM. Column temp. 260°C, isothermal (see Experimental Section). Peak identities are given in Table I. IS = internal standard.

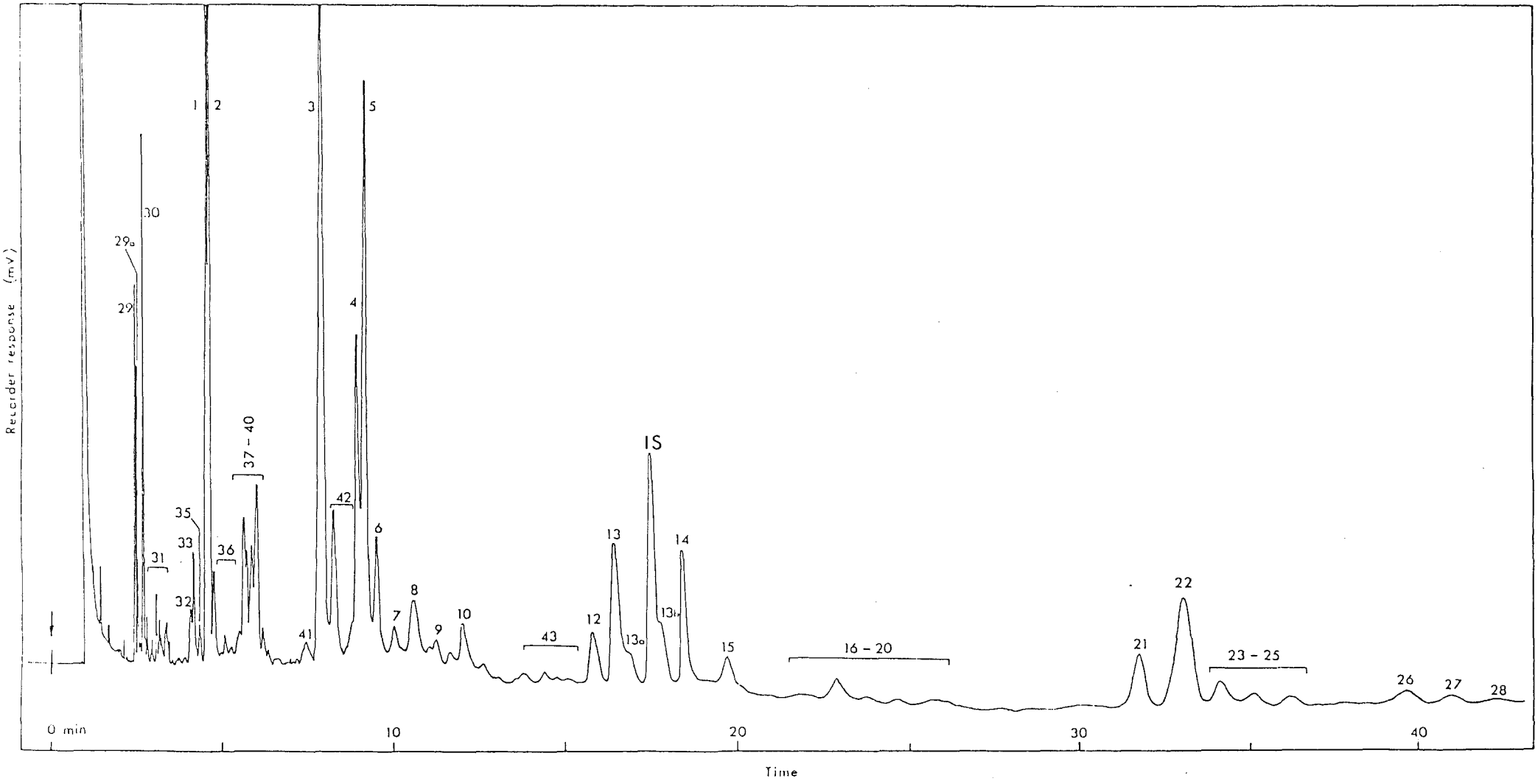


Figure 5. Gas chromatogram of PAH in domestic open-fire soot. Column temp. 260°C, isothermal (see Experimental Section). Peak identities are given in Table I. IS = internal standard.

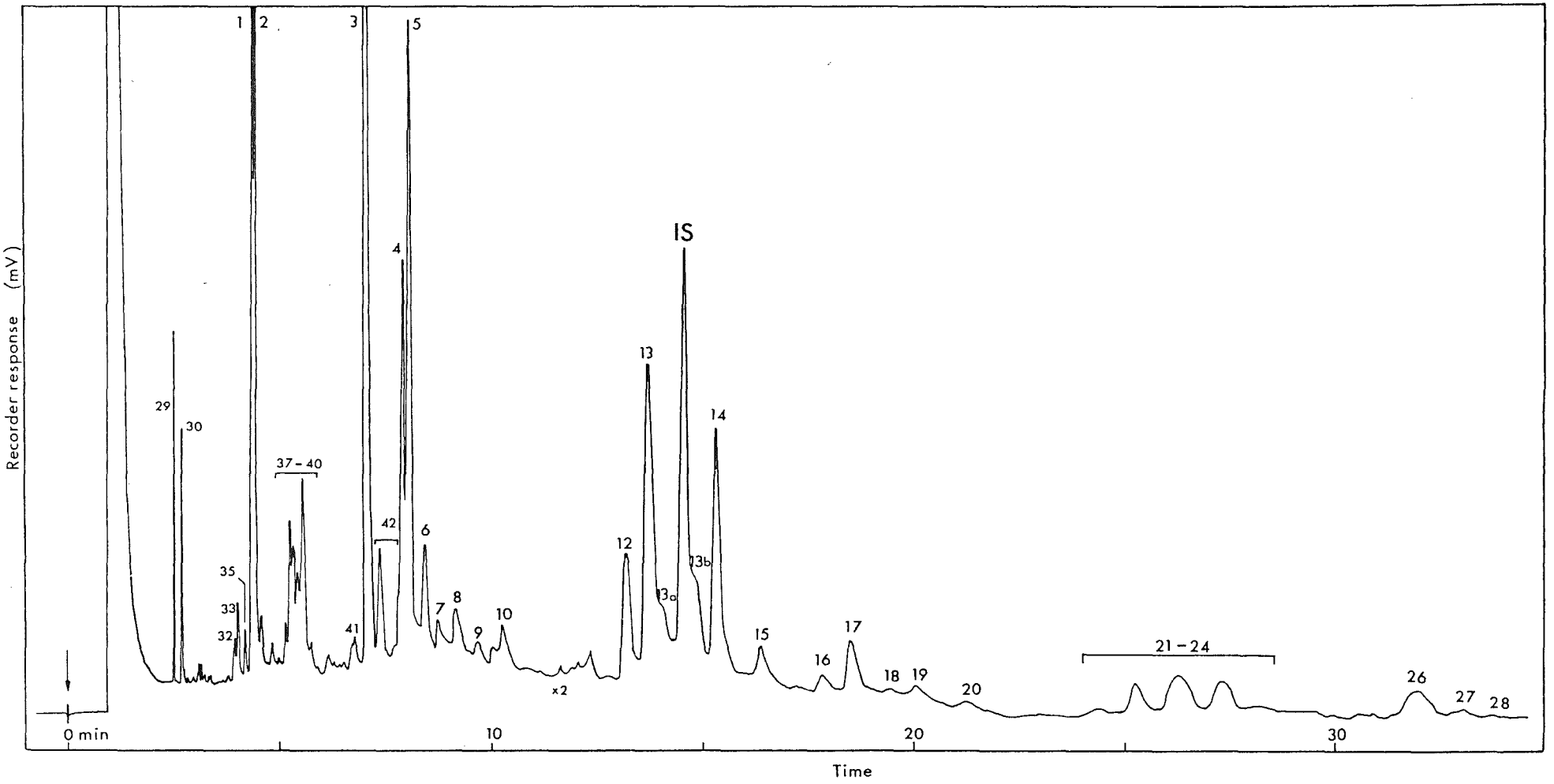


Figure 6. Gas chromatogram of PAH in a typical Heathcote/Avon River and estuary mud sample. Column temp. 260°C, isothermal (see Experimental Section). Peak identities are given in Table I. IS = internal standard.

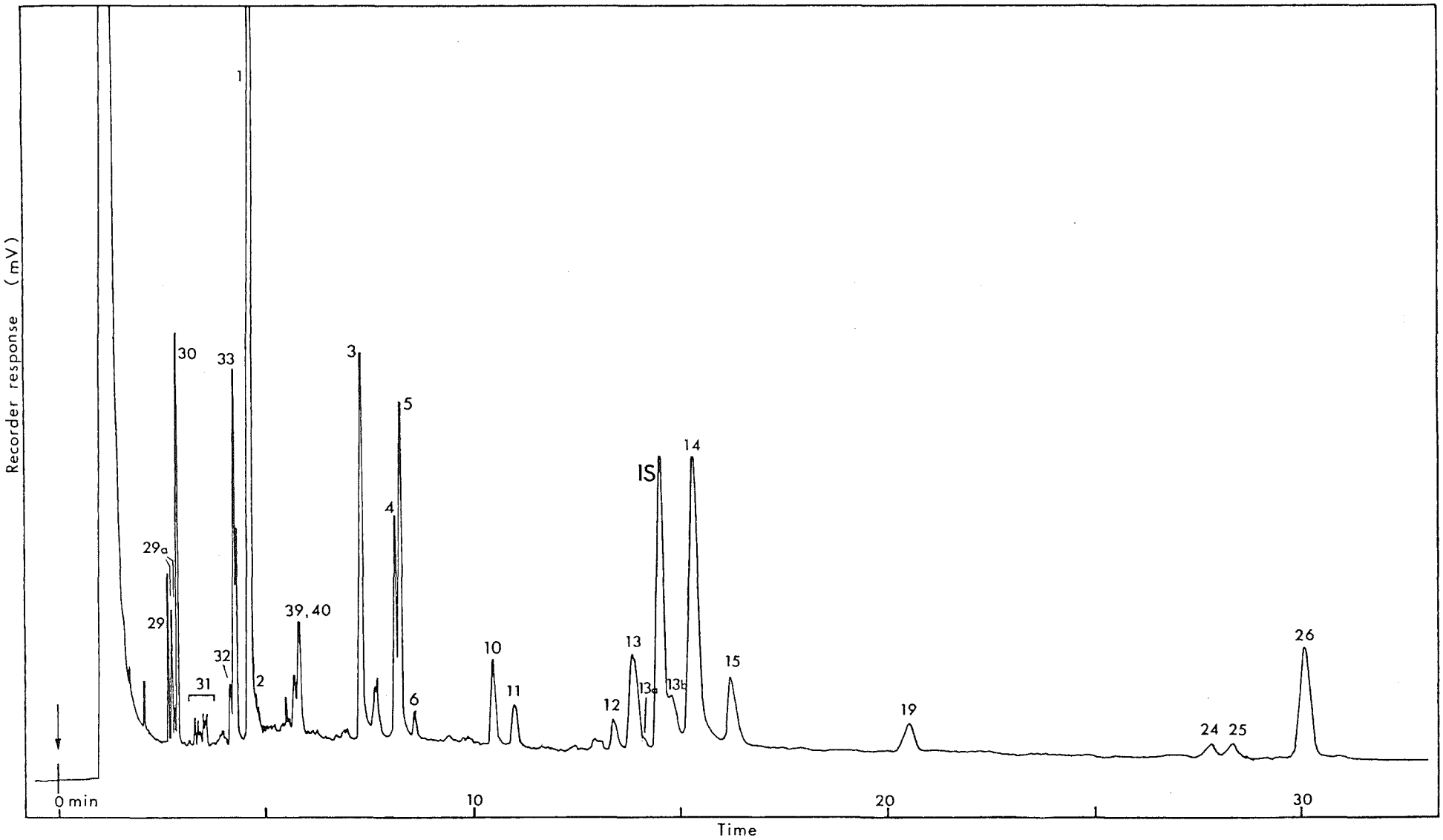


Figure 7. Gas chromatogram of PAH in automobile exhaust. Column temp. 245° ⟶ 270° C (see Experimental Section). Peak identities are given in Table I. IS = internal standard.

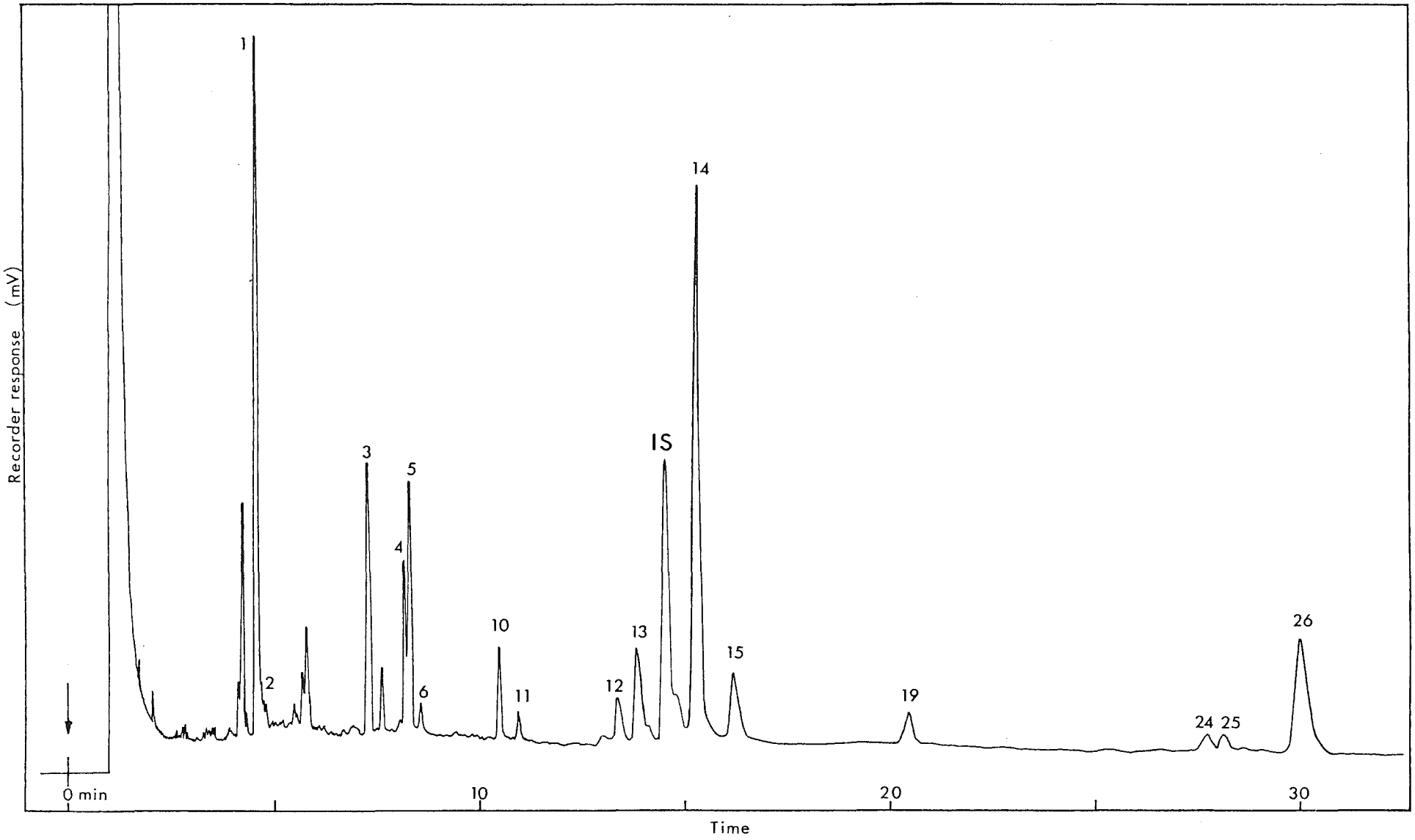


Figure 8. Gas chromatogram of PAH in car park building APM. Column temp. 245° → 270°C (See Experimental Section). Peak identities are given in Table I. IS = internal standard.

was a compromise which enabled a complete analysis to be carried out in less than 40 min while at the same time allowed the satisfactory resolution of the critical isomers.

The stationary phase (OV-101) used in this work is, however not suitable for separating the three isomers of benzofluoranthenes - [k] (non-carcinogenic[95] - but see ref. 32) and [b],[j] (carcinogenic[32,95]) at the moderately high column temperatures used. Nevertheless, it is possible to partially resolve one isomer from the other two which co-elute at a lower column temperature (ca. 150°C, isothermal), or alternatively, by using an OV-17-coated capillary column (at ca. 240°C, isothermal)(Figure 9). The elution characteristics possessed by the benzofluoranthenes on the two stationary phases permit the estimation of their relative concentrations in a particular sample. On OV-101, the [b] and [j] isomers co-elute as a single peak, whereas on OV-17 it is the [j] and [k] isomers that have the same retention time.[83] By analysing a sample twice, on OV-101 and OV-17 columns at the respective temperatures, it is thus possible to determine the contributions of each isomer to the total benzofluoranthene content in that sample. As an example, it was established that the [b] and [j] isomers constitute approx. 70 percent of the total benzofluoranthene concentration of an Avonside airborne particulate matter sample and an Avon River mud sample. Generally, no attempt was made to resolve and thus quantify these isomers individually in each sample; only the total benzofluoranthene was measured. (The two most widely used stationary phases

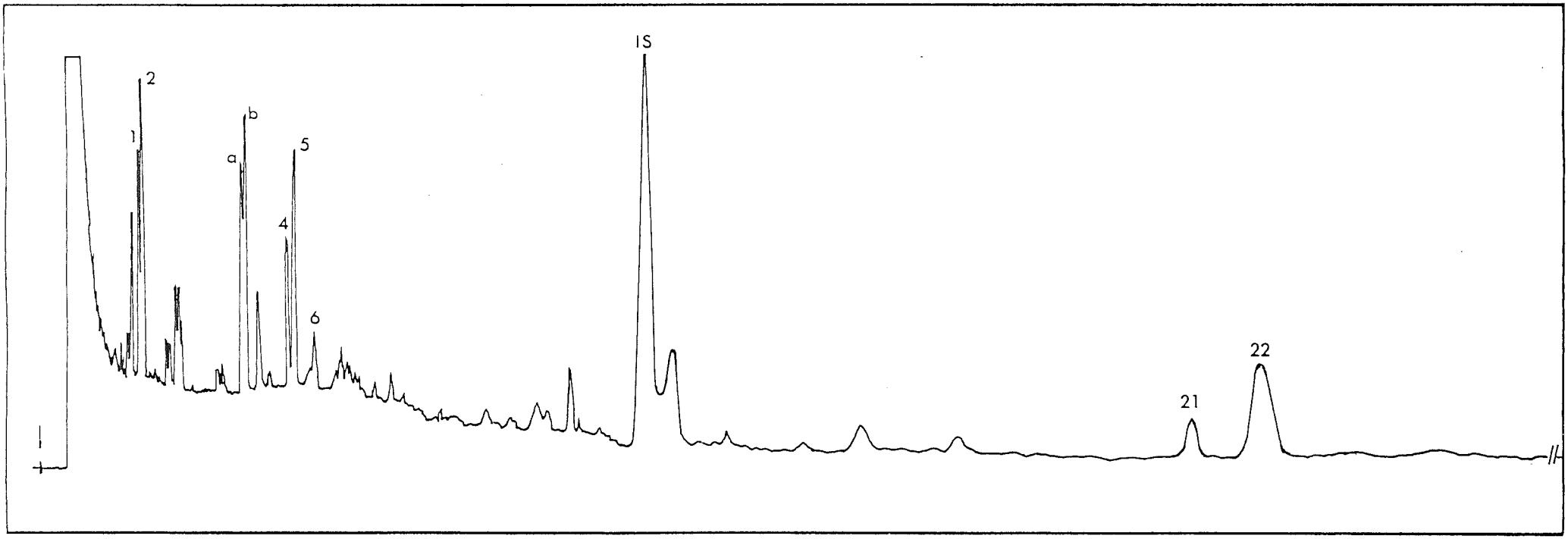


Figure 9. Gas chromatogram of PAH in Avonside APM, obtained from an OV-17-coated SCOT column (30 m x 0.5 mm i.d.). Column temp. 240° C, isothermal. Other conditions were similar to those of OV-101 analyses. Note the partial separation between benzo[j], [k]fluoranthenes and the [b] isomer. See Table I for identities of other components.

for capillary column PAH determination are SE-52 and SE-54;[7,42] SE-54 can partially resolve all three benzofluoranthenes at carefully controlled column temperature conditions,[46] but under the normal analytical conditions, both phases can only separate benzo[b]fluoranthene from the [j] and [k] isomers which elute as a single peak.[6,7,12,38,43,44,46,47,88,96-104]

The benz[a]anthracene/chrysene peaks actually encompass a third isomer, triphenylene, which has the same retention time on OV-101 and OV-17 as chrysene.[83] These two can be resolved by using a capillary column coated with Poly S 179 (polyphenyl ether sulphone) stationary phase.[42] However, since both are non-carcinogenic, their non-resolution on OV-101 is not crucial in this study.

The tentative identification of the carcinogenic dibenzanthracenes ([a,c],[a,h] and [a,j]) was made by utilising retention time data (no reference compounds were available). Their identities were confirmed by GC-MS. Resolution of the [a,c] and [a,h] isomers was not possible, however, although with both being carcinogenic, this was not considered essential.

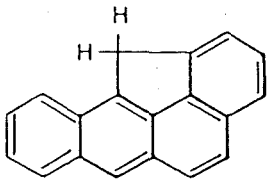
While the major components are all parent (i.e. unsubstituted) PAH, nearly all of the minor peaks consist of alkylated compounds, especially the methyl isomers. All the minor peaks were characterized by GC-MS, after tentative identification of some of them by available retention time data.

Components 37 and 38 each have a molecular mass (Mr) of 242 amu which identifies them as the methyl derivatives of chysene and/or benz[a]anthracene. The specific isomers

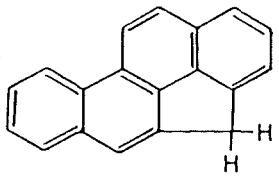
responsible for these peaks could not be ascertained from their mass spectra. However, doping studies using 4-methylchrysene indicated that this sterically-hindered PAH was not present (it eluted just after peak 38). The absence of this PAH in urban atmosphere has previously been reported.[71] All the methylchrysenes (six possible isomers) are at least moderately carcinogenic,[32,40] so it may not be essential that they be resolved and identified. The same cannot be said of the methylbenz[a]anthracenes, however, because not all of them are carcinogenic.[32,40] It was not possible to establish the positions of methyl substitution of these isomers with the techniques used in this work. Pulse Fourier-transform ^{1}H nuclear magnetic resonance spectroscopy[71] and capillary column GC-MS (with mixed charge exchange-chemical ionization)[53] have been used to solve this problem although even then the positions of methyl substitution could not be determined with certainty.

For the assignment of identities to peaks 39 and 40 (Mr 240), several possibilities must be considered: the methyl derivatives of benzo[ghi]fluoranthene and cyclopenta[cd]pyrene, and the four possible $C_{19}H_{12}$ isomers, dibenzo[def,i]fluorene (I) 4H-cyclopenta[def]chrysene (11), 4H-cyclopenta[def]triphenylene (III) and 4H-benzo[fg]pyrene (IV).[46]

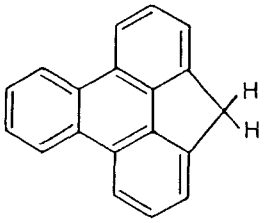
The mass spectra for both components corresponding to peaks 39 and 40 showed very high intensity $(M-1)^{+}$ ions (*m/z* 239) (approx. 90 percent of the base peak) - this



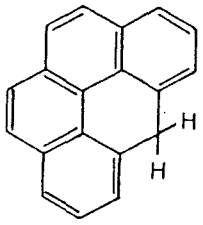
I



II



III



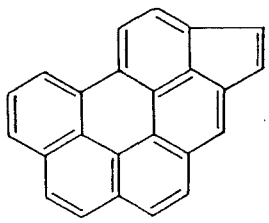
IV

would suggest the absence of methylbenzo[ghi]fluoranthene and methylcyclopenta[cd]pyrene because the intensity of the $(M-1)^+$ ion of monomethylated PAH is often less than that of methylene PAH. Nevertheless, an $(M-15)^+$ ion, although of low intensity, was observed in both spectra, so the presence of the methyl derivatives mentioned cannot be completely dismissed. A fairly prominent *m/z* 254 ion was also observed in the mass spectrum of component 40, possibly indicating the presence of binaphthyl.

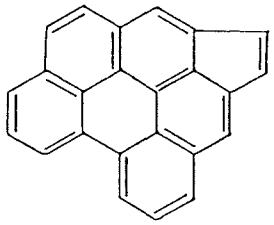
It is interesting that the series of peaks just described (peaks 37 - 40) has a similar pattern of occurrence for airborne particulate matter (APM) (from all sites, including Manchester Street), domestic soot and mud samples (Figures 3 - 6). Car park building (CPB) and

automobile exhaust samples (which are representative of definitive traffic pollution) on the other hand, show a different profile with relatively more of the methylene compounds (I - IV) (peaks 39,40) than the methylchrysenes and methylbenz[a]anthracenes (peaks 37,38) (Figures 7,8) in any particular sample. This difference in relative concentrations of methyl and methylene derivatives between the above two groups of samples can be extended to include the similarly substituted benzofluoranthenes and benzopyrenes (peaks 7 - 11). Components 7 - 9 (Mr 266) are the methylbenzofluoranthenes and methylbenzopyrenes and are characteristic of APM, soot and mud samples (Figures 3 - 6). CPB and exhaust samples contain only small quantities of these compounds. On the other hand, the latter two types of samples feature prominently the methylenebenzopyrenes (Mr 264, peaks 10 and 11), as shown by Figures 7 and 8. Methylenebenzo[e] pyrene (peak 10) is also present in APM, soot and mud samples but at concentrations not much greater than those of the methylbenzofluoranthenes and methylbenzopyrenes; methylenebenzo[a]pyrene is not detected in these samples. It would appear that the profile of this particular region (peaks 7 - 11) of a PAH gas chromatographic trace can be taken as a reasonably good indicator of whether or not the source from which a sample is collected is very heavily (i.e. CPB samples) or completely (i.e. exhaust samples) dominated by traffic pollution. Almost identical profiles to those shown in Figures 7 and 8 have been obtained by Grimmer, et al[91,105] for automobile exhaust samples, and from samples collected in a city area burdened with traffic emissions.

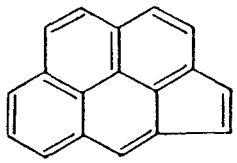
The profile of the dibenzofluoranthenes (Mr 302, peaks 21 and 22) and cyclopentabenzo[ghi]perylenes (Mr 300, peaks 24 and 25) (and also another component which elutes between these two sets of compounds and which gives a mass spectrum with *m/z* 302 and *m/z* 300 ions), also has features peculiar to the type of sample analysed. In soot and APM (again there appears to be no distinction between APM samples collected at different sites) samples (Figures 3 - 5), the dibenzofluoranthenes, especially the isomer (unknown) giving rise to peak 22, are very prominent, with relatively lower concentrations of the cyclopentabenzo[ghi]perylenes. Mud samples (Figure 6) contain approximately the same concentrations of all these components, except that cyclopenta[bc]benzo[ghi]perylene (peak 25, see figure below) is not detected. Automobile exhaust and CPB samples (Figures 7 and 8), however, contain only the cyclopentabenzo-[ghi]perylenes. This result is again in agreement with those of previous studies.[91,105]



Cyclopenta[ef]benzo[ghi]perylene
(Mr 300, peak 24)



Cyclopenta[bc]benzo[ghi]perylene
(Mr 300, peak 25)



Cyclopenta[cd]pyrene

A compound which is considered to be a good indicator of motor vehicle (petrol-engined) pollution is cyclopenta[cd]pyrene.[105c,106-108] Results from this work support this observation. Under the gas chromatographic conditions used here cyclopenta[cd]pyrene possesses the same retention time as benz[a]anthracene. Mass spectrometric analyses of APM, mud and soot samples revealed no trace of this compound (Mr 226).(It is possible that some may be present, but an uncertainty exists because the *m/z* 226 ion observed in the mass spectrum of benz[a]anthracene (Mr 228) may be due to its $(M-2)^+$ ion; for an unsubstituted PAH, a $(M-2)^+$ ion is commonly present (see above). To complicate the situation further, unsubstituted PAH can also lose four hydrogen atoms, giving the $(M-4)^+$ ion. For benz[a]anthracene, this gives a peak of *m/z* 224 which, of course, could also be due to the $(M-2)^+$ ion of cyclopenta[cd]pyrene. The intensities of the *m/z* 224 and *m/z* 226 ions are, however, very low compared to that of *m/z* 228, so it seems unlikely that they arise from cyclopenta[cd]pyrene.) In the automobile exhaust and car park building (CPB) samples, however, cyclopenta[cd]pyrene dominates benz[a]anthracene and chrysene whose concentrations

are almost negligible. Such an observation has also been previously reported for exhaust samples.[105] Often, in this study, only one peak is observed in this region of the gas chromatograms of these samples. Mass spectra of this peak show that the *m/z* 226 ion is by far the most abundant, although at the tail end of the gas chromatographic peak a comparatively low intensity *m/z* 228 ion (absent in the first few spectra taken) is detected, probably due to benz[a]anthracene and/or chrysene as would be expected if they are present.

It is surprising that cyclopenta[cd]pyrene was not detected in (traffic-dominated) Manchester Street 24-h APM samples. A possible explanation for this is that over this extended period of sampling, degradation of the unstable PAH would most certainly have occurred. Losses of PAH, especially those of lower molecular masses (including those eluting before benz[a]anthracene/cyclopenta[cd]pyrene), during sampling are normally expected[109-113] but obviously where a compound exceptionally sensitive to degradation is concerned, the loss is then very much greater. Exposure to irradiation[111-115] (for at least a few hours during sampling) and the multitude of atmospheric pollutants[112] (some of which will be discussed in Section 2.3.1) will most certainly result in losses of the more susceptible PAH. Losses can also be considerable for the more volatile PAH during sampling over long periods of time (due to the "Blow-off Effect").[112,115]

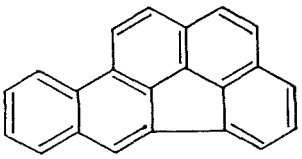
Cyclopenta[cd]pyrene is in fact known to be highly unstable.[105c,106-108] It has been reported[108] that from

APM samples refrigerated in the dark immediately after collection, only 65 percent of this compound was recovered compared with 90 percent of pentacyclic and larger PAH (recoveries of benzo[a]pyrene averaged 80 percent). For the exhaust and CPB samples in this work, the sampling durations normally ranged from ca. 15 min to ca. 2 h respectively so it is perhaps less likely for cyclopenta[cd]-pyrene to degrade to an extent comparable to that for the 24-h samples. In addition, the compound forms such a high proportion of the entire PAH concentration that even allowing for the losses during sampling, there will still be much of it that will be intact and subsequently detected.

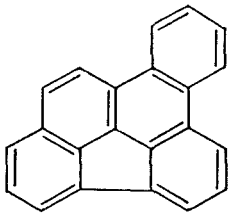
The only other samples in which cyclopenta[cd]pyrene was detected were high-volume (hourly) Manchester Street APM samples. (Table XI, Section 2.3.3 below). These samples were found to contain none of the PAH of lower molecular masses so it is rather surprising that the highly unstable cyclopenta[cd]pyrene should be present. No explanation can be offered for this observation but it may be speculated that perhaps the atmospheric conditions were not conducive to the build-up of PAH during the day of sampling but since cyclopenta[cd]pyrene forms such a large proportion of the PAH content in traffic pollution samples,[105c,106,108] any PAH collected will almost certainly be this compound. Thus, it is one of just five PAH (all others of higher molecular masses) detected (see Table XI). Confirmatory evidence that these hourly samples are traffic-dominated comes from the relatively high levels of benzo[ghi]-perylene (another good indicator of traffic pollution, see below) detected.

The group of minor peaks, collectively labelled 31 in the gas chromatographic traces, consists of compounds having molecular masses of 276 and 278. PAH with the former molecular mass may include dibenzo[b,ghi]fluoranthene (V), dibenzo[b,mno]fluoranthene (VI), dibenzo[a,ghi]fluoranthene (VII), indeno[1,2,3-cd]fluoranthene (VIII), cyclopenta[cd]perylene (IX), acenaphth[1,2-a]acenaphthylene (X) and phenanthro[10,1,2,3-cdef]fluorene (XI). Possibilities for compounds with Mr 278 include dibenz[a,i]anthracene (XII) and pentacene (XIII). All these assignments are only tentative.

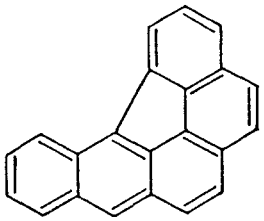
A sulphur-containing PAH, benzonapthhothiophene (Mr 234, peak 35) detected in APM,[44b,47,105b,105c] coal tar,[46] automobile exhaust emissions,[105c] lake sediments,[90] fish tissue[116] and water[101] by other workers, has also been found in this study in some samples (mainly APM and mud, see Figures 3-6). Benzo[b]naphtho[2,1-d]thiophene (XIV) is generally indicative of domestic fuel (coal) and diesel-engined exhaust pollution,[105c] but mass spectral data did not permit positive identification of this compound in this work. The mass spectrum does, however, show the presence of an ion of *m/z* 236 [M^+:$(M+2)^+$ ratio 14.29 observed; 16.74 calculated)], due to the ^{34}S isotope. A second Mr 234 component (which elutes before the first mentioned) is also detected, close to benzo[c]phenanthrene and this could be benzo[b]naphtho-[2,1-d]thiophene [M^+:$(M+2)^+$ 13.60]; this assignment is consistent with literature retention time data,[90,92] and if correct would mean that the first Mr 234 component may possibly be benzo[b]naphtho[2,3-d]thiophene (XV).[116]



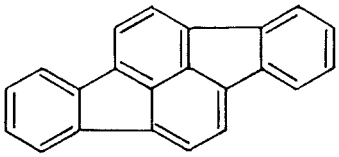
V



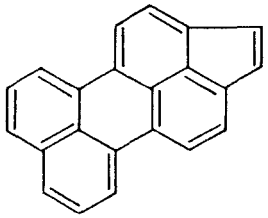
VI



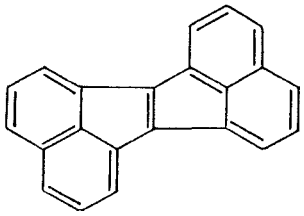
VII



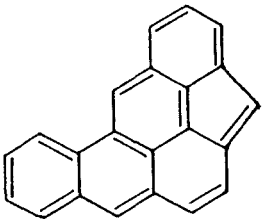
VIII



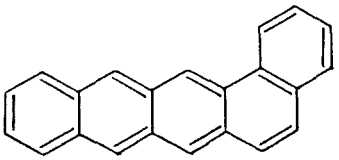
IX



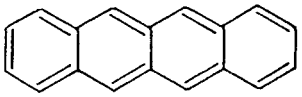
X



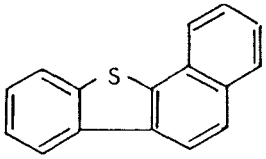
XI



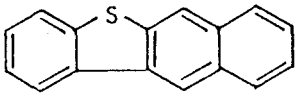
XII



XIII



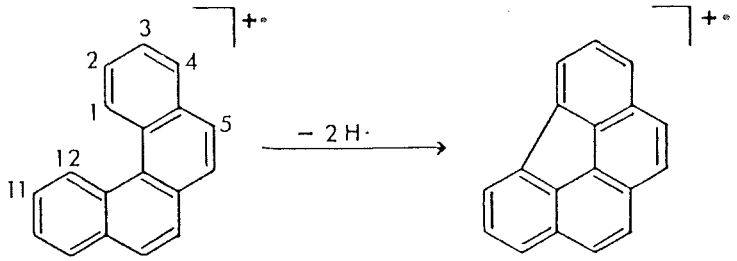
XIV



XV

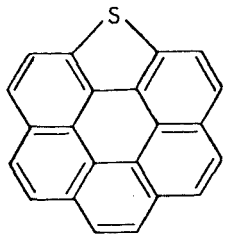
Apparently, benzo[b]naphtho[2,1-d]thiophene is not present in petrol-engined automobile exhaust emissions.[105c] Only petrol-engined vehicle emissions were considered in this study and none of the samples were found to contain components of Mr 234; this result thus agrees with the published observation.

The presence of the carcinogenic benzo[c]phenanthrene in all samples has been confirmed by GC-MS. This compound (Mr 228, peak 32) has a structure which facilitates the loss of two protons from the 1 and 12 carbons to form the benzo[ghi]fluoranthene ion [equation (1)].[42] The mass spectrum of benzo[c]phenanthrene shows a very prominent *m/z* 226 ion, in contrast to the spectra of other PAH of the same molecular mass (benz[a]anthracene, chrysene, etc.).



m/z 228 *m/z* 226 (1)

Two very minor components not actually detected by FID (flame ionization detection)-GC but observed on the total ion current traces, and for which mass spectra were obtained, have molecular masses of 306 (see Table I, peaks 21 and 22) and 326 (which elutes before the dibenzofluoranthenes). The component of Mr 306 may possibly be a sulphur-containing PAH with the tentative



XVI

structure XVI which has been proposed[96,107] for a compound with an identical molecular mass and a similar relative retention time, and found in carbon black extracts. Mass spectra of this component showed the presence of an *m/z* 308 ion [of M^+:$(M+2)^+$ ratio 13.70 observed; 13.66 calculated for $C_{22}H_{10}S_1$], indicating that this compound is very likely to be a sulphur-containing PAH.

2.2.2 PAH gas chromatographic profiles

As discussed in the preceding section, samples collected from different sources show some obvious differences in their PAH gas chromatographic profiles. In particular, car park building (CPB) and automobile exhaust samples can be easily distinguished from APM, soot and mud samples by considering the profiles of (i) the methylbenzofluoranthenes and methylbenzopyrenes, and the methylenebenzopyrenes (peaks 7 - 11, Figures 3-8). Another difference that can be discerned by visual inspection is the benzo[ghi]perylene concentrations in these two sets of samples. This component (peak 14) occurs in very high concentrations in exhaust and CPB samples in relation to the other compounds, as will be further discussed in the following section.

Profiles of APM and soot samples on the one hand and mud samples on the other show only a minor difference - this involves the dibenzofluoranthenes and cyclopentabenzo[ghi]-perylenes (peaks 21 - 25), especially the component (dibenzofluoranthene) responsible for the very prominent peak 22 in soot and APM samples, as pointed out in the previous section.

The PAH profiles for APM from different sites are very similar to that for domestic soot. This would be understandable in the case of Avonside where the pollution is predominantly domestic (see Section 2.1.6). However, even though empirical considerations would indicate that Manchester Street is a traffic-dominated area and Bealey Avenue a mixed (traffic/domestic)-source location, their respective profiles are not very different from those of Avonside or soot. There may be a slight difference in the concentrations of benzo[ghi]perylene relative to other components between Manchester Street and Avonside samples but this is usually not conclusive on a cursory examination of the profiles. The gas chromatographic traces shown in the previous section clearly indicate that Manchester Street profiles do not resemble those of exhaust or CPB.

2.3 QUANTITATIVE ANALYSIS OF PAH

In general 28 PAH eluting from benz[a]anthracene (and cyclopenta[cd]pyrene) to the dibenzopyrenes inclusive have been quantified. Some of these are minor components

but their identities have generally been established fairly conclusively (see Section 2.2.1) from mass spectrometric analysis. Quantification was not attempted on the components whose identities at this stage are still tentative. These include the PAH of Mr 240 and 242 (see Table I). Another series of components not quantified was that which elutes before benz[a]anthracene. While the identification of these is almost certainly correct, their stability under the airborne particulate matter (APM) sampling conditions used is uncertain (see Section 2.2.1) It was felt that since their concentrations could be unreliable (i.e. giving a false representation of their occurrence in the environment), quantitation was undesirable. Cyclopenta-[cd]pyrene, although an unstable PAH, was quantified out of necessity because of its chromatographic coincidence with benz[a]anthracene. It is a major component of automobile exhaust, car park building (CPB) and Manchester Street high-volume (hourly) APM samples but is not detected, or is present only at low levels, in other APM, soot and mud samples. For these latter samples, the quantification of benz[a]anthracene would therefore include cyclopenta[cd]-pyrene (if present at all) while for the first set of samples, the reverse is true.

2.3.1 Source identification of city and suburban PAH

In Tables II - IV are listed the levels of individual PAH determined for APM samples collected over 24-h periods at the Manchester Street, Avonside and Bealey Avenue sites.

Table II. PAH and Pb Concentrations over Selected 24-h Periods at Manchester Street ([APM] > 100 $\mu g/m^3$)

	Date(day/mth)	27/7	3/8	4/8	6/8	7/8	11/8	14/8	16/8	17/8	18/8	22/8	23/8
	Wind	SW	NE→SW	SW→NE	Calm	NE→SW	SW	NE→SW	Calm	SW	SW→NE	Calm	NE
	Total APM(mg)	10.5	10.7	11.0	15.5	10.1	9.6	9.9	15.4	9.6	12.3	13.2	13.8
	APM($\mu g/m^3$)	141	147	154	217	138	155	134	213	120	158	166	174
	PAH(ng/m^3)	110	236	246	371	136	161	125	358	120	123	291	241
	Pb($\mu g/m^3$)	3.5	3.8	2.4	5.1	3.5	3.7	2.6	3.8	3.0	3.7	3.5	3.7
Peak No.*	Individual PAH (ng/m^3)												
1	BaA	16	9	20	36	8	10	6	29	6	5	18	17
2	Chr	7	6	8	15	4	4	4	15	3	3	9	7
3	BF	11	22	28	45	18	17	14	45	13	16	29	21
4	BeP	4	17	14	19	6	9	8	19	8	9	18	8
5	BaP	8	15	18	32	10	13	11	38	11	12	20	17
6	Pe	3	3	4	9	3	2	2	9	3	2	5	5
7	MeBF,MeBP	1	3	3	10	2	1	2	7	2	2	4	4
8	MeBF,MeBP	3	7	9	18	5	5	4	15	5	4	13	8
9	MeBF,MeBP	1	14	10	17	6	9	4	8	3	3	11	8
10	MethBeP	3	8	6	11	3	4	3	9	3	1	9	6
12	DBajA	3	5	6	12	4	5	3	14	4	5	9	8
13	IP	6	9	13	20	12	10	9	21	8	8	24	14
14	BPe	14	16	28	24	11	19	12	33	14	17	23	25
15	An	3	4	7	11	1	6	5	10	4	3	7	7
16	MeBPe,etc.	1	10	4	5	1	5	3	4	1	1	4	5
17	MeDBA	2	8	5	12	5	6	4	9	2	3	13	9
18	MeDBA	-	1	1	2	1	2	1	2	-	1	2	2
19	MeDBA	2	3	2	5	3	2	1	4	1	2	6	4
20	MeDBA	1	1	1	5	2	2	-	2	1	1	6	3
21	DBF	3	11	9	12	5	4	4	10	2	3	9	10
22	DBF	6	21	16	27	11	9	8	26	6	6	21	20
23	DBF,CBPe	3	11	5	7	5	3	5	5	3	2	11	7
24	CBPe	1	5	11	4	1	2	2	5	2	2	5	5
25	CBPe	1	5	2	2	2	2	2	5	3	2	4	4
26	Co	6	16	14	7	6	7	5	9	9	7	8	10
27	DBP	1	6	4	4	1	2	3	5	3	3	3	7

See Table 1 for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 28 (See Table I) were not detected.

Table III. PAH and Pb Concentrations over Selected 24-h Periods at Avonside ([APM] > 100 $\mu g/m^3$)

	Date(day/mth)	8/7	9/7	10/7	11/7	18/7	20/7	22/7	23/7
	Wind	Calm	Calm	Calm	Calm	NE	Calm	Calm	Calm
	Total APM(mg)	30.8	9.6	24.0	12.2	13.2	15.9	21.0	24.4
	APM($\mu g/m^3$)	373	107	275	132	141	183	238	301
	PAH(ng/m^3)	871	184	584	271	349	440	535	799
	Pb($\mu g/m^3$)	2.3	1.1	3.3	2.0	2.3	3.2	3.7	4.1
Peak No.*	Individual PAH (ng/m^3)								
1	BaA	89	9	37	16	19	61	62	88
2	Chr	55	7	26	9	10	27	35	56
3	BF	105	26	76	35	46	48	74	105
4	BeP	28	9	22	14	17	17	22	41
5	BaP	71	19	57	23	29	36	70	66
6	Pe	21	4	15	6	7	9	10	14
7	MeBF,MeBP	23	4	11	6	7	9	10	11
8	MeBF,MeBP	30	9	26	11	14	23	23	36
9	MeBF,MeBP	46	8	18	9	11	14	17	23
10	MethBeP	38	7	18	7	10	12	13	19
12	DBajA	20	7	22	9	12	11	16	23
13	IP	31	9	31	16	20	17	26	43
14	BPe	33	11	37	18	22	21	28	37
15	An	18	4	15	6	10	9	12	12
16	MeBPe,etc.	8	3	7	3	5	3	6	10
17	MeDBA	25	9	23	10	13	14	16	22
18	MeDBA	7	2	11	2	4	3	4	7
19	MeDBA	13	4	12	5	6	8	10	11
20	MeDBA	4	3	6	3	5	3	2	6
21	DBF	31	11	26	10	15	21	11	35
22	DBF	68	3	60	28	37	46	35	74
23	DBF,CBPe	30	6	9	6	9	7	10	18
24	CBPe	28	3	3	5	5	7	9	13
25	CBPe	23	1	1	3	4	5	4	8
26	Co	8	4	9	8	9	5	6	13
27	DBP	17	2	6	3	3	4	4	8

See Table I for an explanation of abbreviations

* PAH corresponding to peak nos. 11 and 28 (see Table I) were not detected.

Table IV. PAH and Pb Concentrations over Selected 24-h Periods at Bealey Avenue ([APM] > 100 $\mu g/m^3$)

	Date(day/mth)	8/7	9/7	10/7	11/7	18/7	22/7	23/7
	Wind	Calm	Calm	Calm	Calm	NE	Calm	Calm
	Total APM(mg)	17.9	11.8	23.7	12.7	10.8	10.1	25.1
	APM($\mu g/m^3$)	316	115	274	134	114	230	287
	PAH(ng/m^3)	569	251	728	249	225	697	786
	Pb($\mu g/m^3$)	5.0	2.7	6.4	2.8	2.8	4.2	6.0
Peak No.*	Individual PAH (ng/m^3)							
1	BaA	35	11	74	24	19	78	80
2	Chr	25	13	42	16	9	71	46
3	BF	75	37	82	35	30	85	107
4	BeP	23	14	31	10	10	18	32
5	BaP	55	25	57	19	20	53	72
6	Pe	13	3	15	6	4	9	14
7	MeBF,MeBP	12	3	11	6	3	9	15
8	MeBF,MeBP	27	6	24	11	8	26	35
9	MeBF,MeBP	22	10	22	7	6	20	32
10	MethBeP	15	7	17	8	3	18	20
12	DBajA	15	8	22	6	6	20	22
13	IP	27	14	35	11	11	34	35
14	BPe	35	17	49	18	16	38	37
15	An	12	2	24	6	6	16	19
16	MeBPe,etc	3	2	6	2	2	5	8
17	MeDBA	18	11	24	10	6	18	25
18	MeDBA	5	3	5	1	1	2	2
17	MeDBA	18	6	15	3	3	10	11
20	MeDBA	4	4	2	1	2	7	4
21	DBF	25	9	37	8	10	29	31
22	DBF	56	29	66	21	25	61	80
23	DBF,CBPe	11	8	20	7	6	21	18
24	CBPe	16	2	15	3	4	12	11
25	CBPe	7	1	9	2	3	11	7
26	Co	10	4	17	5	7	18	15
27	DBP	5	2	7	3	5	8	8

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 28 (see Table I) were not detected.

Table V. Comparative Levels (ng/m^3) of Selected PAH in some Cities of the World

	Budapest[117] (Range, winter)	Calgary[118] (Mean, city centre)	Los Angeles[119] (Geom. mean, year)	New York City[60] (composite samples, winter)	Toronto[63] (Mean, year, at suburban site)	Antwerp[120] (Mean, winter)	Rome[121] (Mean, autumn/ winter)	Iidabashi, Tokyo[122] (Mean, summer)	Christchurch[a] (Range, winter)
PAH									
BaA	10.4-776.0	0.09	0.18			~ 22 (+ Chr)	3.8	7.8	5 - 89
BaP	9.7 - 55.9	0.12	0.46	1.15 - 1.3	0.65	~ 28 (+ BeP + Pe)	3.2	2.9	8 - 72
BbF		0.20 (+ BkF)	0.54	1.7 (+ BjF , BkF)	1.60 (+ BkF)	~ 30 (+ BjF , BkF)	9.4 (+ BjK , BkF)		11 - 107 (+ BjF , BkF)
IP		0.31	1.34			~ 1			6 - 43
BPe	0.9 - 18.0	1.01	3.27	0.9	5.7	~ 3		6.3	11 - 49

See Table I for an explanation of abbreviations

[a] This study; values taken from Manchester Street, Avonside and Bealey Avenue 24-h APM samples (Tables II - IV)

Also tabulated are the lead concentrations associated with each sample. From the tables it may be seen that PAH levels can reach high values in the Christchurch atmosphere. As a comparison, the levels of selected atmospheric PAH (all weakly to strongly carcinogenic, see Appendix A) in other parts of the world are presented in Table V. With the possible exception of Budapest, all the other cities show lower levels of PAH than Christchurch.

The wind data in Tables II - IV show that the highest PAH levels are usually found during calm conditions in the city. The latter situation normally prevails when a temperature inversion layer blankets the city, a condition the occurs reasonably frequently in Christchurch (usually from early evening to mid-morning) during the winter season (May - August).[1 2 3] In an inversion layer, the air is stable and its vertical movement is restricted, preventing any pollution trapped within the layer from moving into higher altitudes and being dispersed. Strictly speaking, there are light surface winds as the inversion layer begins to form, but surface drag tends to slow the winds down, facilitating further cooling and strengthening the inversion which in turn further reduces turbulence.[1 2 3] Even then, due to the high surface roughness of an urban area, there will be enough turbulence to permit some degree of atmospheric mixing.[1 2 3] (This phenomenon most probably accounts for the lack of any outstanding differences between the PAH gas chromatographic profiles of Manchester Street, Avonside and Bealey Avenue APM samples.) Fortunately, however,

conditions conducive to the formation of inversion layers in Christchurch do not usually persist for more than a few days, ensuring the dissipation of pollution after this period of time.

The identification of the sources of PAH emissions into the atmosphere was and still remains an important part of PAH studies. To this end, various attempts have been made to determine the relationships between individual PAH components in samples whose sources are known. Knowledge of such correlations could subsequently be used as a guide to ascertain the possible source or sources of the PAH in a particular sample. The use of coronene as an indicator of automobile exhaust emissions because of its great abundance in such samples was first suggested in 1962.[124] In particular, it was suggested that low benzo[a]pyrene to coronene ([BaP]/[Co]) ratios would indicate that the sample was collected from a site dominated by automobile exhaust pollution whereas a high ratio would suggest pollution by domestic fuel (coke, coal, wood, for example) emissions.

Benzo[ghi]perylene (BPe) is another PAH associated with automobile exhaust emissions, and it has been used by investigators[125-127] in relation to BaP as a source indicator of PAH emissions. It has been stated[105c] that BPe is one of the two most abundant PAH found in petrol-engined automobile exhaust emissions (cyclopenta[cd]pyrene is the other). BPe also forms a high proportion of the total PAH measured in traffic-polluted Los Angeles, California, USA.[127] Quantitative results from the present work support this observation.

It was previously mentioned that no major differences in the PAH gas chromatographic profiles were observed for the three sites represented in Tables II - IV. However, [BaP]/[BPe] ratios calculated from the data in the tables are consistent with the empirical observations made earlier (Section 2.1.6) that Avonside is dominated by domestic fuel pollution and Manchester Street by vehicular traffic pollution. [BaP]/[BPe] ratios for Bealey Avenue show that it is influenced more by domestic fuel than traffic emissions. A plot of [BaP] vs. [BPe] for all three sites is shown in Figure 10. The lines are obtained by linear least squares fit of [BPe] on [BaP] allowing for errors in both sets of parameters.[129] The slope of the line of best fit for Manchester Street is greater than that for Avonside. Bealey Avenue lies in between the two, agreeing with the observation that this site has a mixture of domestic fuel and traffic pollution although closer inspection of Figure 10 reveals that the slope for this site is closer to that for Avonside indicating a greater contribution by domestic pollution. Statistical analysis on the slopes show that all three are significantly different at the 99 percent confidence level.

Analysis of [BaP]/[BPe] data points for all three sites reveals that they deviate from a normal distribution. In spite of this, an analysis of variance,[130] which is still applicable since the deviation was found to be very slight, was carried out. A single-variable test of variance (see Appendix B) on the data support the conclusions derived from Figure 10: Manchester Street and Avonside [BaP]/[BPe] ratios are significantly different at the 1 percent level [F_{cal} 40.96 (F_{tab} 8.29)]; so are Manchester Street and

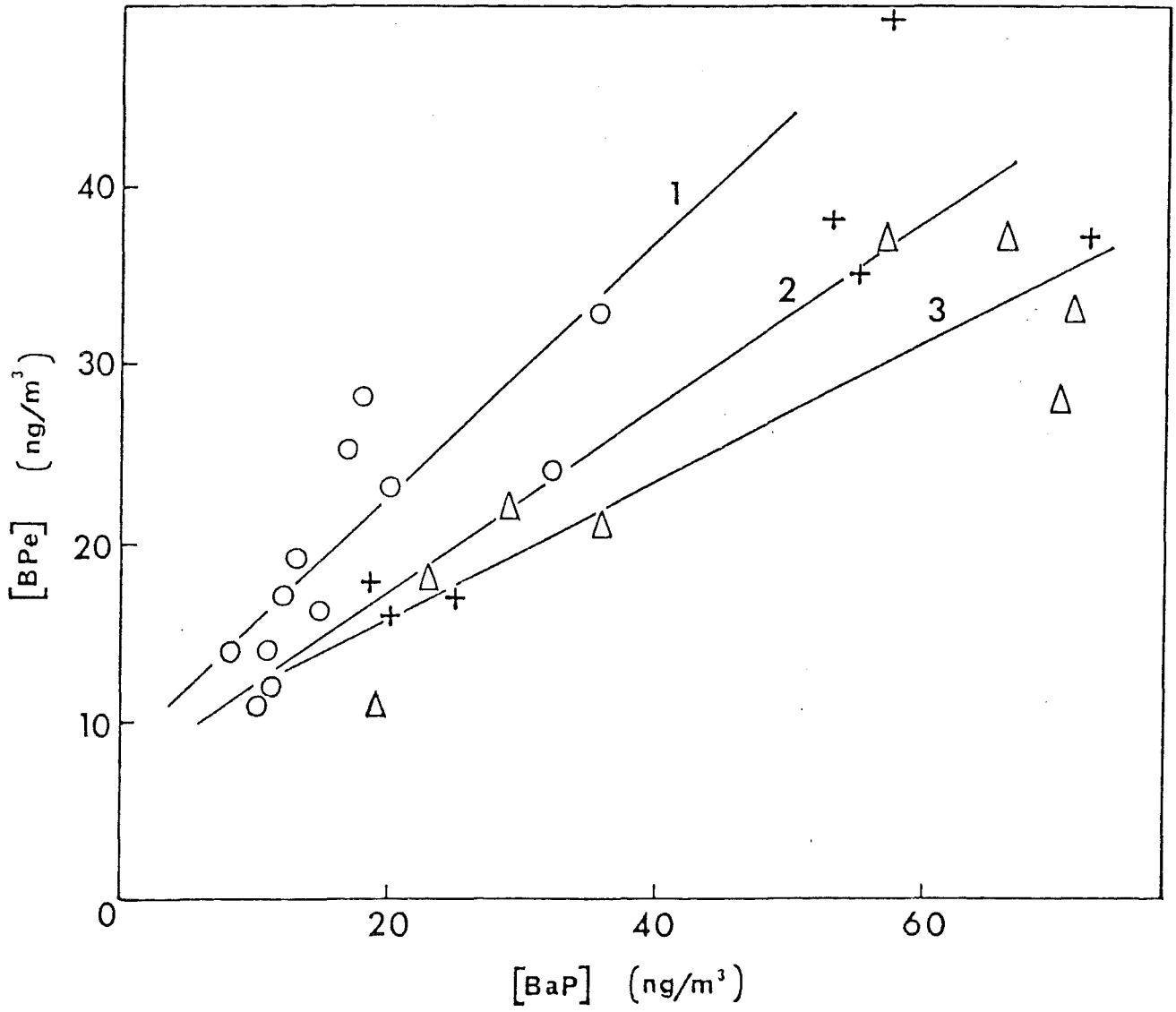


Figure 10. Plot of [BaP] vs [BPe] for 24-h APM samples from Manchester Street (O), Avonside (Δ) and Bealey Avenue (+). 1: Manchester Street, slope 0.71, std. dev. of slope 0.084; 2: Bealey Avenue, slope 0.57, std. dev. of slope 0.096; 3: Avonside, slope 0.39, std. dev. of slope 0.078.

Bealey Avenue ratios [F_{cal} 21.98 (F_{tab} 6.11)], whereas Avonside and Bealey Avenue ratios are not distinguishable at that same significance level. [All F values (variance ratios) obtained in this study are listed in Appendix B (Tables XVIII and XIX)].

A set of data not normally distributed can sometimes be made to conform to a normal distribution by a suitable transformation.[131,132] For the [BaP]/[BPe] ratios, a logarithmic ($\log_{10}$) transformation was found to normalize the distribution, and the $\log_{10}$[BaP]/[BPe] values were analysed as before to give F values very similar to those obtained from the untransformed [BaP]/[BPe] ratios. While confirming the earlier relationships obtained for the three sampling sites, this test also shows that the application of variance analysis is legitimate in cases where a data set is slightly deviant from a normal distribution (in other words, the F value is insensitve to a minor aberration,[131,132] as experienced in this case).

Instead of analysing [BaP]/[BPe] ratios as described in the preceeding paragraphs (i.e. one-variable analysis), a joint-analysis[130] which considers two variables simultaneously (that is, individual [BaP] and [BPe] values) may be carried out (see Appendix B). Such a multivariate test is normally a better test of discrimination than a one-variable analysis.[130] While no improvement in discriminating power was observed in this case when the test on (untransformed) [BaP] and [BPe] values was performed, the results nevertheless provide additional evidence that confirms the earlier conclusion

that Bealey Avenue and Avonside samples cannot be differentiated from each other (at the 1 percent significance level) on the basis of their [BaP] and [BPe] values.

A plot such as that in Figure 10 is of limited use as an indicator of the source of PAH if only one sample is available, although the simple [BaP]/[BPe] ratio can provide a convenient, if tentative, means of source identification. Yet, as illustrated by Bealey Avenue samples, difficulties can arise because the use of such ratios does not provide a means sufficiently sensitive to indicate mixed-source emissions, in which there is preferential contribution from a particular source.

The reportedly high reactivity of BaP has introduced some reservations about using it as a reference for source identification. Several workers have studied the susceptibility of BaP to photochemical decomposition,[111,114] oxidation by ozone,[111,114,133] peroxyacetyl nitrate (PAN)[134] and nitration by nitrogen dioxide[133] or generally, oxides of nitrogen (NO_x).[134] Ozone, PAN, nitrogen dioxide and NO_x are of course all present as pollutants in the atmosphere. Some of these experiments were carried out with BaP placed in petri dishes,[114] or adsorbed on soot particles,[134] and subjected to real and simulated atmospheres. The other studies[113,134] were carried out using BaP-entrained filters. The general conclusion from these investigations is that BaP on different matrices can undergo degradation under normal atmospheric conditions. Although a recent study[135] appears to indicate that BaP artificially adsorbed from the vapour phase onto coal fly ash suffers no photochemical decomposition on this substrate,

it is reasonable to assume, and it is generally accepted that BaP adsorbed on APM in the atmosphere is prone to degradation, if not photochemically, then by other means. Losses of BaP adsorbed on APM and collected on filters during high-volume sampling has been shown to occur.[109-113,115] Whether degradation occurs prior to sampling or on the filter, the lack of stability of this PAH would make it an unsuitable choice as a component of a relationship to determine the source of PAH pollution. It has been suggested[105c] that by using the ratio [BaP]/[BeP], where BeP is benzo[e]pyrene, a measure of BaP degradation in the atmosphere or during sampling may be estimated; barring any BaP losses, the range for common emissions[105c] (coal stoves, diesel and petrol engines, coke plants and oil burners) should be 0.5 - 1.5. However, inspection of the [BaP]/[BeP] ratios for all the atmospheric APM samples (Tables II - IV in this Section and Tables IX - XIII in Section 2.3.3 below) analysed in this work shows that, according to this test, the degradation of BaP was insignificant; this observation would support the use of [BaP]/[BPe] ratios as a convenient means of identifying PAH sources, as has been done thus far. On the other hand, because of the well-documented high reactivity of BaP and perhaps also because the [BaP]/[BeP] test of BaP degradation may not be strictly applicable to the Christchurch atmosphere (the study cited was carried out in the Federal Republic of Germany), it is advantageous to evaluate other relationships which will not only act as reliable indicators of PAH source emissions, but also give even better discrimination than

[BaP]/[BPe] ratios, while at the same time eliminating or at least reducing the uncertainties associated with the use of BaP. The approach adopted towards the achievements of these aims involves the consideration of lead levels associated with each APM sample.

Lead is of course a major environmental pollutant. About 5.45×10^8 kg of the metal are emitted into the atmosphere per year world-wide and over 62 percent of this is attributed to automotive sources (both 1971 figures),[136] which utilize lead compounds (tetraethyl lead and tetramethyl lead) to raise the octane rating of the hydrocarbon fuel mixture. Previous studies,[137-141] including two[137,140] recently undertaken in Christchurch, have shown that atmospheric lead is closely related to motor vehicle density.

The role of motor vehicles in contributing to the airborne lead content assumes an even greater magnitude in Christchurch because petrol in New Zealand has an average lead content (all grades considered) of ca. 0.78 g/L - higher than that in other countries in Western Europe, North America and Japan. It has been estimated[137] that the only significant source (accounting for 99 percent) of lead in the Christchurch atmosphere is the combustion of lead-containing petrol. Lead emitted from burning New Zealand coal is considered to be negligible, when compared to that from automobiles.[142] Moreover, in Christchurch itself, most of the coal is used industrially, so there is control over smoke and ash emission by the use of precipitators. There is one major industry in Christchurch based on lead, a battery works. The emission

of lead is localized (in Woolston) in this case and should not contribute greatly to the overall level of the metal in the city atmosphere. Various minor sources of atmospheric lead including paint burning and stripping, scrap metal processing and combustion of used sump oil from motor vehicles are not believed to be significant contributors.[137]

A great risk to health involving APM is the inhalation of these particles which are deposited in the human respiratory tract. Respirable particles are considered as those having a diameter of below 5 μm.[143] In general, both the PAH and lead are associated with similarly-sized APM,[126a,144] with the major proportion of these particles lying within the respirable range and therefore representing the most serious health threat. That PAH and lead are deposited on particles of similar sizes is an important result because it means that atmospheric life-times of the APM carrying them are the same so that these pollutants can legitimately be related to each other.

In carrying out these analyses, two variables were used and found to be very satisfactory indicators of PAH source emissions - the total concentration of the PAH, [PAH], corresponding to peaks 1 - 28 (see Table I, Section 2.2.1) and the total lead concentration, [Pb], of each of the APM samples. Specifically, $\log_{10}([PAH]/[Pb])$ values give a sensitive and discriminating indicator of source emissions. A logarithmic transformation of the raw [PAH]/[Pb] ratios was required because of their non-normal

distribution, for a more rigorous statistical analysis. However, as a first approximation, bearing in mind that F values are insensitive to slight deviations from normally distributed data (see above), untransformed [PAH]/[Pb] ratios for Manchester Street, Avonside and Bealey Avenue sites were initially tested using the one-variable analysis method. The results are that while Manchester Street/ Avonside and Manchester Street/Bealey Avenue samples can be distinguished at the 1 percent significance level, Avonside/ Bealey Avenue samples can only just be separated at the 5 percent significance level (see Table XVIII, Appendix B).

There is no doubt about the discrimination between the logarithmically transformed [PAH]/[Pb] ratios when they are analysed for the three sites. Differences between Manchester Street/Avonside and Manchester Street/Bealey Avenue are highly significant at the 1 percent level (F_{cal} 44.03 and 15.92 against F_{tab} 8.29 and 8.40 respectively). The Avonside/Bealey Avenue sites, it will be recalled, were distinguished only at the 10 percent significance level when $\log_{10}$([BaP]/[BPe]) values were tested, but with $\log_{10}$([PAH]/[Pb]) values, discrimination was significant at the 2½ percent significance level (F_{cal} 9.31; F_{tab} 6.41) and even at the 1 percent level (F_{tab} 9.07). Figure 11 shows the distribution of samples for the three sites according to their $\log_{10}$([PAH]/[Pb]) values.

The very strong discrimination between Manchester Street and Avonside samples as shown by $\log_{10}$([PAH]/[Pb]) values can be rationalized by the fact that in a traffic-dominated area, the lead levels in the atmosphere are very

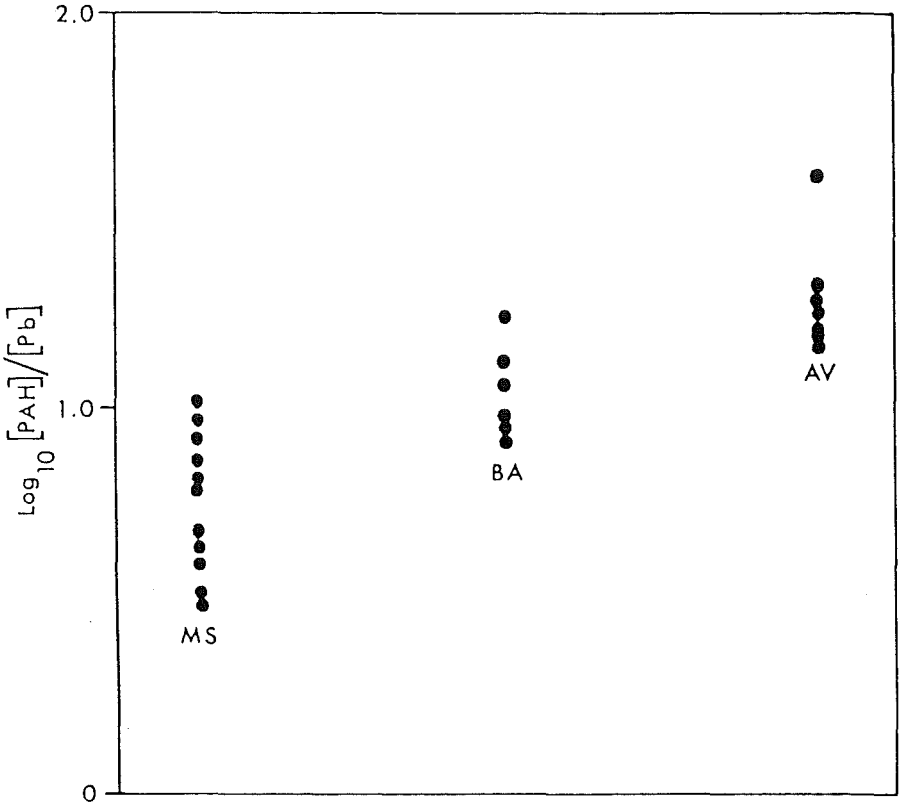


Figure 11. Log_{10}([PAH]/[Pb]) values for Manchester Street (MS), Avonside (AV) and Bealey Avenue (BA) 24-h APM samples.

high. This is especially so in Christchurch where it has been established that virtually all of the airborne lead is derived from petrol combustion in vehicle engines, with negligible contributions from other sources. Log_{10}([PAH]/[Pb]) values for Manchester Street are therefore characterized by lower values than their Avonside counterparts. F_{cal} values for Manchester Street/Bealey Avenue and Avonside/Bealey Avenue sites show again that Bealey Avenue has mixed domestic/ traffic emission sources but with domestic pollution being

the more dominant contributor. (See Table XVIII, Appendix B for calculated and tabulated F values.)

Examination of Figure 11 shows that one point for the Avonside distribution {$\log_{10}$([PAH]/[Pb]) = 1.5783} is not among the main cluster. The possibility that this point is an invalid measurement was tested by the procedure given by Bauer,[145] and found to be such. The one-variable analysis was then repeated for all three sets of samples without this point; the F_{cal} values show that the discrimination between Manchester Street and Avonside samples, and Manchester Street and Bealey Avenue samples is as good as that obtained with the deviant point included (42.29 and 17.56 compared to 44.03 and 15.92 respectively; F_{tab} = 8.40 at the 1 percent significance level. Note that the denominator degrees of freedom are now identical for both data sets). There is a slight improvement (F_{cal} 11.30 compared to 9.30 previously) in discrimination between the Avonside and Bealey Avenue samples.

The use of [PAH]/[Pb] ratios, apart from being more sensitive and discriminating than the [BaP]/[BPe] ratios should also be a less uncertain means of source identification. Although the concentration of BaP is included in the total PAH level, the overall stability of the PAH that are quantified should be higher than that of BaP alone in a particular sample, since most of the other 4- to 7-ring PAH are reasonably stable compounds. Total PAH concentrations and hence [PAH]/[Pb] ratios should therefore be less erratic than BaP concentrations and [BaP]/[BPe] ratios. An obvious

advantage arising from the use of [PAH]/[Pb] is that samples need not be analysed immediately after collection, something which appears to be necessary if [BaP] is used, because of its high reactivity. In the same vein, photodegradation during sample collection (especially during the summer season when it is warm and sunny) can be responsible for substantial losses of BaP from filters.[115] The exercise of source identification should therefore be subject to less ambiguity when total PAH concentrations are used.

2.3.2 Exhaust emissions, car park building APM and domestic soot

The discrimination obtained between the three sampling sites by using [PAH]/[Pb] ratios (discussed in the previous section) encourages the view that the empirical observations about the major sources of PAH pollution at each of these sites are correct. However, to verify that high and low $\log_{10}$([PAH]/[Pb]) values are truly representative of domestic and traffic sources respectively, two additional sets of samples were analysed. Domestic open-fire soot (Table VI) and automobile exhaust emissions (Table VII) should reflect the extreme ends of the PAH pollution spectrum on the basis of their $\log_{10}$([PAH]/[Pb]) values, and as shown in Figure 12, which is the same as Figure 11 except that $\log_{10}$([PAH]/[Pb]) data for exhaust and soot samples have been included, this is the case.

It may be argued that because the exhaust samples were collected while the vehicle engines were idling (i.e. no dynamometer was used), they would not be representative of

Table VI. PAH and Pb Concentrations in Domestic Open-Fire Soot

	Sample	1	2	3	4	5	6	7	8	9	10	11	12
	Fuel	Coal/wood	coal/coke	coal	demol. wood	wood	demol. wood	fencing wood	coal	coal	coal	coal	coal
	PAH (ppm)	99	249	644	330	113	108	324	588	18	1272	162	883
	Pb (ppm)	222	51	101	1024	180	5534	3026	56	121	81	61	43
Peak No.*	Individual PAH (ppm)												
1	BaA	7	40	97	53	15	12	45	101	2	96	7	49
2	Chr	13	22	187	72	21	20	76	152	2	64	7	44
3	BF	21	39	117	81	20	28	52	88	6	186	21	63
4	BeP	6	13	28	18	7	8	15	19	2	39	5	26
5	BaP	11	22	30	41	8	10	31	41	3	242	13	58
6	Pe	3	5	12	7	4	4	6	11	-	13	1	14
7	MeBF,MeBP	4	5	14	5	4	3	5	9	-	14	2	19
8	MeBF,MeBP	3	8	12	4	3	3	5	20	-	38	4	28
9	MeBF,MeBP	1	3	8	2	4	2	11	7	-	52	4	51
10	MethBeP	2	7	6	4	2	3	4	8	-	16	3	12
12	DBajA	5	7	13	8	3	2	7	12	1	15	4	34
13	IP	8	14	21	12	5	5	12	16	1	77	9	27
14	BPe	5	7	15	9	4	2	7	10	1	29	14	24
15	An	1	3	3	4	1	1	2	4	-	12	4	9
16	MeBPe,etc.	1	2	5	-	1	1	4	5	-	38	6	29
17	MeDBA	1	6	6	-	2	1	5	10	-	103	31	103
18	MeDBA	-	1	2	-	-	1	1	2	-	29	6	42
19	MeDBA	-	1	4	-	1	-	2	7	-	11	2	15
20	MeDBA	-	1	4	-	1	-	2	5	-	4	-	8
21	DBF	1	6	12	1	1	-	7	15	-	-	-	-
22	DBF	2	20	20	2	4	1	13	27	-	151	13	174
23	DBF,CBPe	1	5	11	2	1	1	4	6	-	8	4	5
24	CBPe	1	4	8	2	1	-	3	5	-	6	-	trace
25	CBPe	1	2	4	1	-	-	2	2	-	trace	-	trace
26	Co	1	4	2	1	-	-	1	2	-	10	-	18
27	DBP	-	2	3	1	-	-	2	4	-	19	2	31
28	DBP	-	trace	trace	-	-	-	trace	trace	-	trace	-	trace

See Table I for an explanation of abbreviations

*PAH corresponding to peak no.11 (see Table I) was not detected.

Table VII. PAH and Pb Concentrations in Automobile Exhaust Emissions

	Sample	1	2	3	4	5	6	7	8	9	10	11
	PAH (ppm)	13801	384	8028	4018	805	2644	2881	540	1520	724	3364
	Pb($\times 10^3$ppm)	220	301	207	123	466	155	53	376	357	497	291
Peak No.*	Individual PAH (ppm)											
1	BaA/CYC	2215	19	1370	618	23	606	634	11	68	55	443
2	Chr	1160	13	717	331	12	319	334	7	35	28	234
3	BF	456	20	224	174	30	137	354	28	48	45	81
4	BeP	428	18	231	681	40	102	188	30	60	34	85
5	BaP	732	19	280	226	17	136	216	16	37	81	95
6	Pe	176	10	103	37	3	40	71	2	6	10	15
7	MeBF,MeBP	11	5	26	7	5	12	59	4	2	9	2
8	MeBF,MeBP	29	2	28	18	4	27	49	2	4	9	3
9	MeBF,MeBP	23	4	25	22	5	21	30	3	4	17	4
10	MethBeP	465	9	252	90	24	56	44	10	43	24	107
11	MethBap	167	1	83	44	1	21	24	1	2	8	42
12	DBajA	303	11	140	141	15	43	67	29	30	13	35
13	IP	889	20	392	232	42	91	203	49	77	32	133
14	BPe	3403	126	1818	533	281	369	296	151	631	184	960
15	An	695	trace	387	238	12	153	64	11	18	18	236
19	MeDBA	456	6	254	109	19	120	28	8	41	17	128
24	CBPe	190	4	117	55	11	32	11	17	30	9	50
25	CBPe	257	2	98	51	7	21	8	8	29	5	35
26	Co	1747	95	1483	411	254	338	201	153	355	126	676

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 16-18,20-23,27 and 28 (see Table I) were not detected.

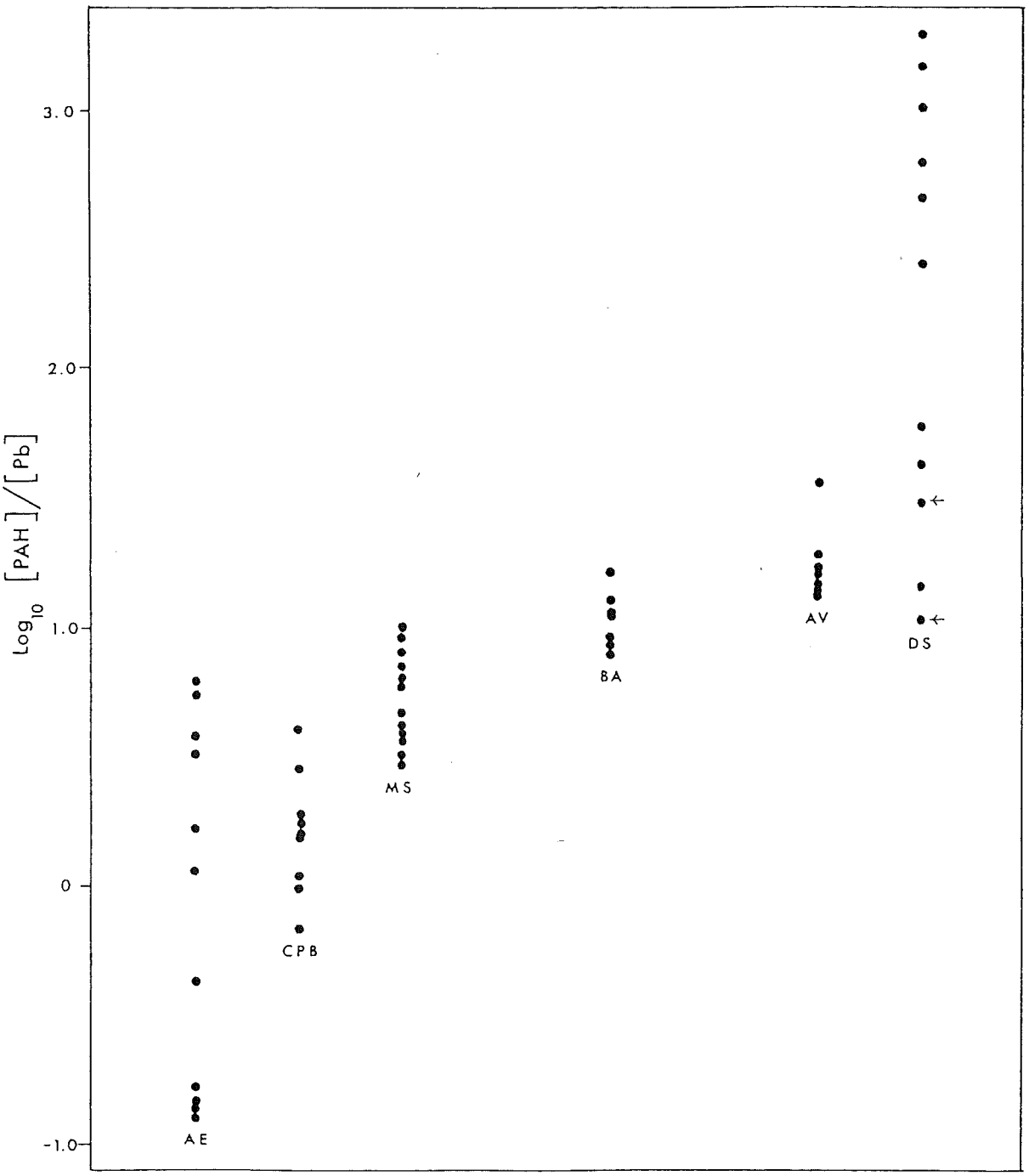


Figure 12. Log_{10}([PAH]/[Pb]) values for domestic soot (DS), automobile exhaust (AE) and car park building (CPB) samples, as superimposed on Figure 11. DS points arrowed refer to samples which contained high lead levels (see text and Table VI). Value for DS Sample no.6 has not been included in this plot.

emissions under normal driving conditions. However, it is PAH concentrations relative to those of lead which are of interest, not the absolute concentrations of either pollutant. The omission of a dynamometer is therefore not critical. Another point that may be made is that the Christchurch city area is served by a considerable number of traffic signal systems. It is therefore very likely that stationary vehicles forming queues in the vicinity of traffic signal zones would be contributing a reasonable proportion of the overall exhaust emissions into the atmosphere.

An attempt to sample automobile exhaust emissions directly by placing a filter within a glass tube into which the exhaust fumes were discharged was found to be unsatisfactory (see Experimental Section). Apart from the deformation of the filter holder due to high exhaust temperature, another problem was that the particulate matter collected showed enormously high lead levels (up to 45 percent by weight) but almost negligible concentrations of PAH. The high lead levels may be explained by an observation, reported in previous studies,[146] that airborne lead concentrations fall off rapidly with distance from the road. Day[137] has also reported a similar phenomenon, although this was for lead in dust samples. Presumably, the high lead levels obtained in the sampling procedure using the glass tube described above were due to the contribution by the lead-adsorbed particulates which would normally be deposited almost immediately after emission from the motor vehicle. It had been hoped that the use of the large sampling chamber

finally adopted for exhaust particulate collection would permit the deposition of a large proportion of the exhaust particulate matter so that only the fraction that under normal conditions would be dispersed as APM (airborne particulate matter) was sampled. Because the sampling chamber was almost entirely a closed system, this sampling scheme was not completely successful. Particularly, the lead levels obtained were still very high. However, from the point of view of PAH sampling, the method was considered satisfactory because the problems of using the filter monitors (holders) in a high temperature environment were eliminated. A better evaluation of this method of sampling is to compare the quantitative results obtained from this method with those from normal high-volume sampling in car park buildings (CPB) (Table VIII). CPB samples can be considered as reasonably representative of pure traffic pollution, since the range of driving conditions that normally occur on city streets are generally present in these buildings. The comparison takes the form of the percentages of PAH and lead in each of the exhaust and CPB samples relative to the total particulate matter collected:

	% Lead	% PAH
CPB	Range: 5.90 - 13.90 Mean: 8.3	0.07 - 0.35 0.16
Auto. Exhaust	12.0 - 50.0 28.0	0.03 - 1.40 0.36

Table VIII. PAH and Pb Concentrations in Car Park Building (CPB) APM

	CPB	Lichfield Street			Oxford Terrace			Manchester Street		
		1	2	3	4	5	6	7	8	9
	PAH (ng/m^3)	374	58	403	101	127	566	766	1008	203
	Pb ($\mu g/m^3$)	19.8	9.0	13.9	9.9	11.7	35.4	40.3	24.8	12.8
Peak No.*	Individual PAH (ng/m^3)									
1	BaA/CYC	56	2	68	5	10	138	143	195	18
2	Chr									
3	BF	22	4	21	6	8	34	41	44	13
4	BeP	19	3	19	5	6	28	30	43	9
5	BaP	23	1	24	7	9	34	50	57	12
6	Pe	6	1	10	2	3	18	11	16	3
7	MeBF,MeBP	1	-	1	-	1	2	3	1	2
8	MeBF,MeBP	2	1	-	-	-	2	1	2	1
9	MeBF,MeBP	2	-	-	-	-	1	2	2	1
10	MethBeP	12	2	12	4	4	12	25	27	13
11	MethBaP	5	1	4	2	1	5	9	9	1
12	DBajA	12	3	10	4	4	19	24	30	6
13	IP	31	6	29	11	12	36	58	70	17
14	BPe	98	20	86	26	28	124	153	213	58
15	An	17	2	31	6	9	46	59	82	10
19	MeDBA	5	2	8	1	2	9	15	22	5
24	CBPe	11	1	9	3	4	7	13	18	3
25	CBPe	5	-	7	3	3	3	12	21	3
26	Co	47	9	64	16	23	48	117	156	28

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 16-18,20-23,27 and 28 (see Table I) were not detected.

Total APM (mg)	24.0	11.6	27.7	14.9	15.3	55.9	24.3	10.6	28.1
APM ($\mu g/m^3$)	242	117	193	137	124	492	290	302	217

It can be seen from the table that the exhaust samples contain a higher average percentage of lead than CPB samples showing that the aim of sampling only the particulates that subsequently become the airborne fraction was not realized by using the sampling chamber. The average percentage PAH level is also higher for the exhaust than CPB samples. Taking these results together, it is clear that although exhaust samples contain more lead, the effect is offset by high levels of PAH, so that the [PAH]/[Pb] ratios do not vary significantly from those obtained under the reasonably normal traffic conditions exemplified by CPB samples. If $\log_{10}$([PAH]/[Pb]) values for CPB samples are included in Figure 12, it is observed that they lie in the same general area of the graph as those of exhaust samples. Moreover, it has been shown (Figures 7 and 8) that the PAH gas chromatographic profiles of these two types of samples are identical. Finally, if a single-variable analysis is carried out on the $\log_{10}$([PAH]/[Pb]) values for these two sets of samples, the F value is found to be 1.56 (F_{tab} 8.29 at the 1 percent significance level) (Table XIX, Appendix B), showing that exhaust and CPB $\log_{10}$([PAH]/[Pb]) values are indistinguishable from each other.

Most work of a similar nature which has been reported[50, 58, 91, 128] is based on samples obtained from vehicles on a dynamometer. The results of this study indicate that the use of this device is not essential to give data typical of normal traffic pollution, especially since only the concentrations of PAH and lead relative to each other are

of interest. Although there is a wide scatter of exhaust $\log_{10}([PAH]/[Pb])$ values, this can be attributed to the different engine conditions of the individual vehicles.

The results for CPB samples (Table VIII) are also of interest in their own right. Being confined places, it is not surprising that CPB tend to suffer from a build-up of PAH to fairly high levels, comparable to high-APM samples (Tables II - IV). All but one of the samples were collected over ca. 2-h periods, the exception being Sample no. 8 which was collected over ca. 30 min on a cool, overcast day with a light drizzle. The weather conditions as well as the time of sampling (4.00 p.m. - 4.30 p.m. when traffic is reasonably heavy in the CPB) probably account for the high PAH level obtained.

The lead levels are very high in comparison with other (non-CPB) APM samples (Tables II-IV, IX-XIII). Again this can be attributed to the enclosed nature of CPB. It is also possible that a proportion of the airborne lead sampled might not have originated directly from motor vehicles at the time of sampling. As discussed earlier, there is deposition of lead-adsorbed particulates in the vicinity of the emission source so that only a fraction of the total particulates will be dispersed as airborne particles. Because of the constant disturbance caused by vehicular movements in CPB, a resuspension of previously deposited particulates is likely (this has been demonstrated by Sehmel,[147] using zinc sulphide particles). This phenomenon, of course does not apply only to CPB; however, in the streets, the average speed of vehicles

is higher and the rate and degree of resuspension is correspondingly enhanced.[147] This, coupled with local wind currents will tend to disperse the particulate matter more widely, and therefore the average level of airborne lead above the street is much lower than inside an enclosed space. It is conceivable that part of the PAH content in a sample may also have originally been adsorbed on fallout particulates which were then resuspended in a similar way. There is perhaps a case for the periodic cleaning of CPB in order to prevent the accumulation of such fallout residues.

Criticisms of non-representativeness may be directed at the domestic soot samples as well, since they were not collected by air filtration as the APM was. However, the soot was taken from the tops of chimneys and hence should be similar in constitution to the particulate fraction dispersed into the atmosphere (and which is sampled by air filtration). This conclusion is supported by the similarity of the gas chromatographic profiles of the PAH of APM and soot samples (as already discussed in Sections 2.2.1 and 2.2.2).

An unexpected problem was encountered when one of the soot samples (Sample no. 6, Table VI) was found to contain a lead concentration of > 5000 ppm, giving a $\log_{10}([PAH]/[Pb])$ value of 0.3010 (not shown in Figure 12) which lies in the traffic pollution zone. Information about the type(s) of fuel used in all the fireplaces concerned had also been collected during the sampling programme. A check revealed that the occupants of the house from which this particular

sample was collected had been using for some years as the main fuel in their fireplace, painted wood from the demolition of old buildings. Moreover, that section of the chimney which included the top had not been swept for several years. The abnormally high lead level must have been derived from the paint which would have been applied in a period when all exterior paint was lead-based. Two other samples also showed fairly high concentrations of lead (Table XII). One was taken from a house in which demolition (painted) wood formed part of the fuel, while wood from painted fencing had been used in the fireplace in the second house. The $\log_{10}([PAH]/[Pb])$ values for both of these samples are understandably lower than expected although a test of validity[145] shows that both are valid measurements. A similar test for Sample no. 6, however, reveals that it can justifiably be omitted from the data set.

As stated earlier, coal combustion is a negligible contributor of airborne lead in Christchurch. It is therefore worthy of attention that those samples showing the expected high $\log_{10}([PAH]/[Pb])$ values are those corresponding to coal or coke burning in the fireplaces concerned. The three anomalous samples with elevated lead content are probably exceptions to the general rule since the burning of paint[137] or painted wood in open-fireplaces cannot be considered to be a widespread practice in Christchurch. Nevertheless, the experience encountered here shows the importance of having obtained full information about the types of fuel used in the fireplaces considered. Abnormal

results are expected when working with environmental samples. Fortunately in this case, such a result was easily accounted for because of the information available.

All things considered, fitting $\log_{10}$([PAH]/[Pb]) for soot, and exhaust and CPB samples into Figure 12 shows that the [PAH]:[Pb] relationship is an excellent indicator of PAH sources (see also Section 2.3.4 below). In practice, this means that, if a sample collected from a randomly-chosen site is analysed, then its calculated $\log_{10}$([PAH]/[Pb]) value can be assigned to the Manchester Street- (if the pollution at the site is dominated by traffic emissions) or Avonside-zone (if the pollution is domestic emissions) (Figure 12) with 99 percent certainty. For a sample collected from a site with mixed-source pollution, the level of confidence associated with the placement of the $\log_{10}$([PAH]/[Pb]) value in the Bealey Avenue-zone, can be expected to be at least 95 percent. As will be evident in the following section, these conclusions hold for samples collected over 24 h, since collection over this period is more accurately representative of the average (daily) pollution at a particular site.

2.3.3 Application of the [PAH]/[Pb] ratio

To test the effectiveness of the [PAH]:[Pb] relationship as an identifier of PAH source emissions, various other APM samples were collected and analysed (Tables IX - XIII), and their $\log_{10}$([PAH]/[Pb]) values calculated. Figure 13 shows a plot of $\log_{10}$([PAH]/[Pb]) values for hourly samples collected on a single day at Avonside (see Table IX for

Table IX. PAH and Pb Concentrations at Avonside: Samples Taken on Same Day (17/8)

	Time	0810-0850	0910-0950	1010-1050	1110-1150	1210-1250 + 1310-1350	1410-1450 + 1510-1550	1610-1650 + 1710-1750
	Temp/°C	5	5→7.5	8.5→11	11.5→14	15.5→15	15.5→14	13→10.5
	Wind	Calm	Calm	Calm	v.sl.NW	v.sl.NW	sl.SW	SW
	Total APM(mg)	15.7	18.8	18.2	14.9	28.1	19.9	15.5
	APM($\mu g/m^3$)	226	267	254	209	198	139	109
	PAH(ng/m^3)	499	612	338	197	180	83	141
	Pb($\mu g/m^3$)	5.9	8.5	5.0	3.2	1.9	0.7	0.7
Peak No.*	Individual PAH (ng/m^3)							
1	BaA	24	36	22	9	20	11	10
2	Chr	9	12	10	7	9	7	5
3	BF	45	55	29	18	18	3	16
4	BeP	32	37	17	9	11	3	10
5	BaP	52	46	25	11	13	4	23
6	Pe	13	18	8	2	2	2	5
7	MeBF,MeBP	12	17	6	2	2	1	1
8	MeBF,MeBP	25	31	12	4	6	3	3
9	MeBF,MeBP	22	26	10	3	4	1	3
10	MethBeP	17	20	7	5	3	1	2
12	DBajA	20	25	16	10	5	5	4
13	IP	22	38	25	12	9	7	9
14	BPe	52	62	39	22	17	5	11
15	An	21	22	11	8	4	3	3
16	MeBPe,etc	6	5	3	4	3	2	2
17	MeDBA	11	15	7	7	5	3	3
18	MeDBA	3	5	1	1	1	1	-
19	MeDBA	6	8	4	5	4	1	1
20	MeDBA	7	6	2	5	1	1	2
21	DBF	15	18	11	8	10	3	5
22	DBF	34	46	29	20	18	6	9
23	DBF,CBPe	16	15	15	10	5	3	4
24	CBPe	10	10	7	5	4	2	3
25	CBPe	8	9	7	4	3	1	2
26	Co	11	20	10	4	2	3	3
27	DBP	5	10	5	2	1	1	2

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 28 (see Table I) were not detected.

Table X. PAH and Pb Concentrations at Manchester Street: Samples Taken on Same Day (11/9)

	Time	0810-0850	0910-0950	1010-1050	1110-1150	1210-1250	1310-1350	1410-1450	1510-1550	1610-1650	1710-1750	1810-1850
	Wind(km/hr)	15	13	13	11	11	28	29	26	31	31	37
	Total APM(mg)	9.8	8.8	8.6	9.0	7.8	13.9	8.4	9.8	12.1	12.3	6.7
	APM($\mu g/m^3$)	167	133	130	136	118	220	126	144	177	186	100
	PAH(ng/m^3)	42	54	31	46	15	28	38	31	76	22	20
	PB($\mu g/m^3$)	3.3	2.7	2.4	3.3	1.1	1.6	0.9	1.1	1.5	1.1	0.4
Peak No.*	Individual PAH (ng/m^3)											
1	CYC	10	29	8	22	5	5	22	16	58	8	14
2	DBajA	1	2	2	3	1	1	1	1	2	1	1
13	IP	4	5	4	5	2	2	2	2	2	2	1
14	BPe	25	16	14	14	6	8	12	11	13	12	3
26	Co	2	2	3	2	1	1	1	1	1	3	1

See Table I for an explanation of abbreviations

*PAH corresponding to all other peak nos. were not detected.

Table XI. PAH and Pb Concentrations at Manchester Street, Avonside and Woolston over a 7-day period

		Manchester Street	Avonside	Woolston
	Date(day/mth)	3-10/9	3-10/9	3-10/9
	Total APM(mg)	25.7	32.2	24.5
	APM($\mu g/m^3$)	78.4	45.8	42.2
	PAH(ng/m^3)	52	94	66
	Pb($\mu g/m^3$)	2.2	0.6	0.5
Peak No.*	Individual PAH (ng/m^3)			
1	BaA	2	6	4
2	Chr	1	4	2
3	BF	6	13	10
4	BeP	4	5	3
5	BaP	5	7	6
6	Pe	2	2	2
7	MeBF,MeBP	1	2	2
8	MeBF,MeBP	1	3	3
9	MeBF,MeBP	1	3	3
10	MethBeP	2	3	2
12	DBajA	1	4	3
13	IP	3	4	3
14	BPe	8	5	6
15	An	2	2	1
16	MeBPe,etc.	-	1	1
17	MeDBA	1	3	2
18	MeDBA	-	1	1
19	MeDBA	1	2	1
20	MeDBA	-	1	1
21	DBA	1	4	1
22	DBA	3	8	4
23	DBF,CBPe	3	3	2
24	CBPe	1	2	1
25	CBPe	1	1	1
26	Co	2	3	1
27	DBP	-	2	1

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 28 (see Table I) were not detected.

Table XII. PAH and Pb Concentrations at Woolston and Avonside: Weekdays compared to weekends

		Avonside		Woolston	
		Weekday	Weekend	Weekday	Weekend
	Date(days/mth)	27-31/8	25-27/8 + 31/8-3/9	27-31/8	5pm 24-27/8 + 31/8-3/9
	Total APM(mg)	16.1	22.0	10.5	9.6
	APM($\mu g/m^3$)	39	50	31	20
	PAH(ng/m^3)	79	131	41	27
	Pb($\mu g/m^3$)	0.34	0.46	0.47	0.22
Peak No.*	Individual PAH (ng/m^3)				
1	BaA	3	8	4	2
2	Chr	2	5	2	1
3	BF	9	17	4	3
4	BeP	5	8	2	1
5	BaP	5	12	4	2
6	Pe	3	5	1	-
7	MeBF,MeBP	3	4	-	1
8	MeBF,MeBP	4	7	1	1
9	MeBF,MeBP	4	6	-	1
10	MethBeP	2	3	-	1
12	DBajA	2	4	2	1
13	IP	3	6	3	1
14	BPe	6	8	3	2
15	An	2	4	1	1
16	MeBPe,etc.	1	2	1	1
17	MeDBA	2	2	2	-
18	MeDBA	-	1	-	-
19	MeDBA	1	2	1	1
20	MeDBA	1	2	1	1
21	DBF	3	4	1	1
22	DBF	8	8	3	3
23	DBF,CBPe	3	5	1	1
24	CBPe	2	4	1	1
25	CBPe	2	2	1	-
26	Co	2	1	1	-
27	DBP	1	1	1	-

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 28 (see Table I) were not detected.

Table XIII. PAH and Pb Concentrations at Manchester Street and Bealey Avenue: Low-level ([APM] < 100 μg/m^3) Air Pollution Sample.

		Manchester Street			Bealey Avenue	
	Date(days/mth)	30,31/7 15,20,24/8	28/7 1,12,13/8	2,8,21/8	6,17,25,17/7	13,14,19,20,26/7
	Wind	SW	NE	?	SW	NE
	Total APM(mg)	25.9	26.5	11.4	25.5	36.6
	APM (μg/m^3)	71	91	50	89	75
	PAH (ng/m^3)	52	57	45	72	152
	Pb(μg/m^3)	1.51	2.13	2.06	1.27	1.56
Peak No.*	Individual PAH (ng/m^3)					
1	BaA	1	2	3	9	16
2	Chr	1	1	2	6	7
3	BF	7	6	6	7	23
4	BeP	2	3	2	6	6
5	BaP	6	6	4	8	11
6	Pe	1	1	1	2	2
7	MeBF,MeBP	1	1	-	-	2
8	MeBF,MeBP	2	4	2	-	6
9	MeBF,MeBP	1	1	-	-	5
10	MethBeP	2	2	2	-	4
12	DBajA	2	2	2	5	3
13	IP	3	4	3	9	7
14	BPe	7	8	8	9	8
15	An	2	1	1	2	3
16	MeBPe,etc.	-	-	1	-	1
17	MeDBA	1	1	1	-	4
18	MeDBA	-	-	-	-	2
19	MeDBA	-	1	-	-	2
20	MeDBA	1	-	-	-	1
21	DBF	2	2	1	3	9
22	DBF	3	4	3	5	16
23	DBF,CBPe	1	1	-	-	4
24	CBPe	1	1	-	-	2
25	CBPe	1	1	-	-	2
26	Co	3	3	3	1	5
27	DBP	1	1	-	-	1

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 28 (see Table I) were not detected.

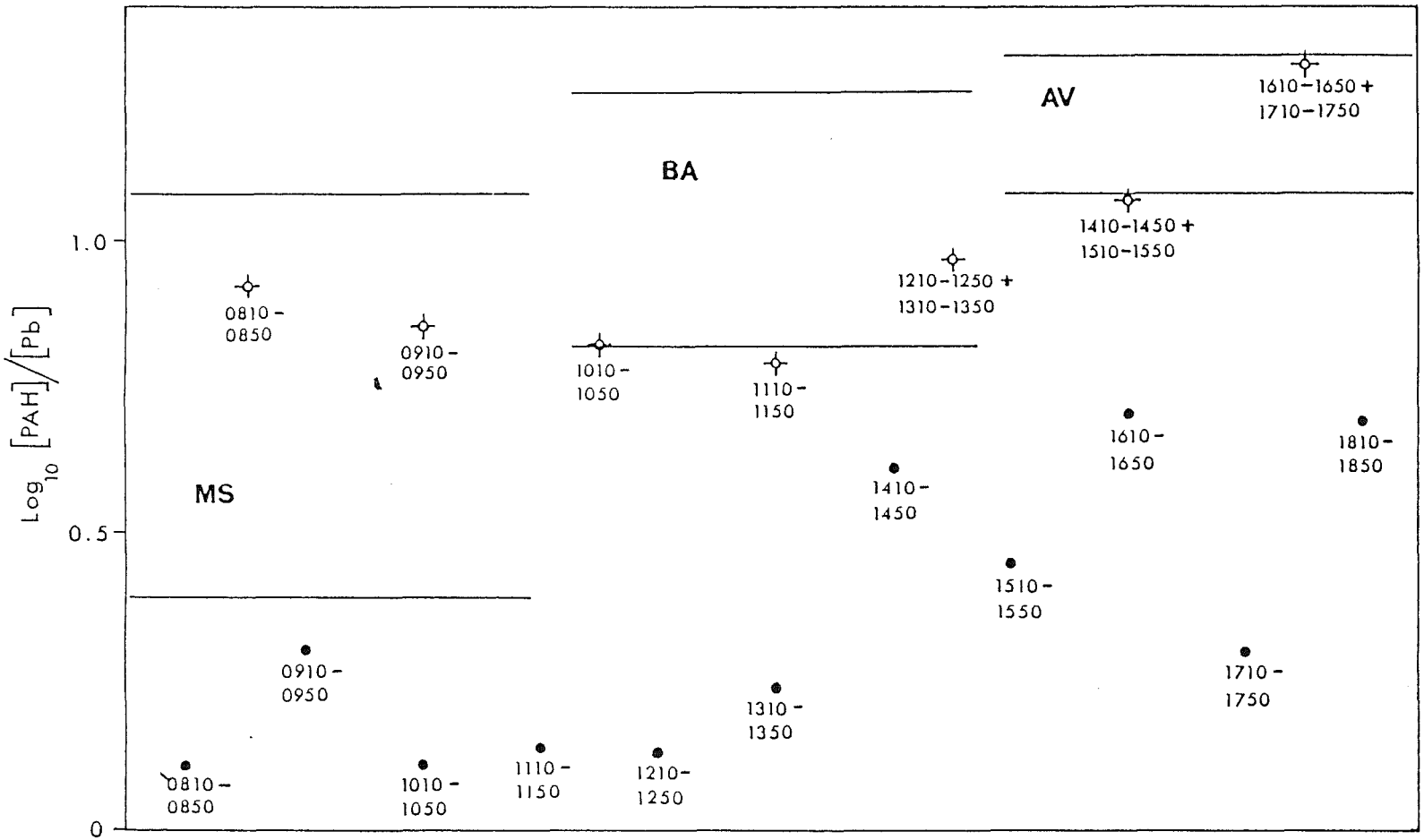


Figure 13. Log_{10}([PAH]/[Pb]) values for hourly Avonside (⊹) and hourly Manchester Street (•) APM samples. Times of sampling are shown next to the points. The horizontal lines represent the spread ($\bar{x} \pm 1.96\ \sigma$) of the log_{10}([PAH]/[Pb]) values for 24-h APM samples from Manchester Street (MS), Bealey Avenue (BA) and Avonside (AV) (see text).

sampling details). The horizontal lines show the upper and lower limits of the distribution frequency of the three sets of $\log_{10}$([PAH]/[Pb]) values for 24-h APM samples from Manchester Street, Avonside* and Bealey Avenue sites (considered earlier in Section 2.3.1). The limits were calculated using $(\bar{x} \pm 1.96\ \sigma)$[148] where $\bar{x}$ = mean, σ = standard deviation, so that 95 percent of the $\log_{10}$([PAH]/[Pb]) measurements for a particular site will lie within the distribution specified for this site as in Figure 13. Based on the results from Section 2.3.1, the limits defined for Manchester Street, Avonside and Bealey Avenue are designated the traffic-zone, domestic-zone and intermediate-zone respectively.

As Figure 13 shows, there is a change in hourly Avonside $\log_{10}$([PAH]/[Pb]) values as the day progresses from early morning to early evening. In the morning, the pollution is in the intermediate-zone (or in the upper region of the traffic-zone). From then on, the increase in the traffic component is evident, but in the early afternoon, the trend is reversed and there is a strong domestic influence on the pollution by the early evening. The pattern of change described fits the observational data on domestic fires in the Avonside area (and in Christchurch residential suburbs in general). Some fires are lit in the early morning and these, coupled with the use of motor vehicles at the same time would place the 0810 - 0850 sample in the intermediate-zone. As the temperature rises during the day, fires are

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* The errant $\log_{10}$([PAH]/[Pb]) value was not used to calculate the Avonside distribution.

allowed to go out and the samples collected during the late morning and early afternoon are traffic-dominated. By late afternoon or early evening, when the majority of fires are lit with the onset of the late afternoon drop in temperature, the pollution shows a strong domestic component. Data for hourly samples from Manchester Street (Table X) were also studied in a similar manner. The $\log_{10}$([PAH]/[Pb]) values were mainly found below the lower limit of the traffic-zone although there was upward shift into this zone in the evening (Figure 13).

Samples collected over seven days (Table XI) (same time period for all) at Manchester Street ($\log_{10}$([PAH]/[Pb]) = 0.3736) and Avonside (1.1950) as expected fall into the traffic- and domestic-zones respectively, whereas a similar Woolston sample (1.1206) lies in the intermediate-zone but also just into the domestic-zone. Woolston, as explained in Section 2.1.6, is an industrial area; the sampling site is ca. 400 m from a rubber mill, which manufactures carbon black-based products. It is interesting to note that although Avonside samples may display slight traffic-dominated or mainly mixed-source (intermediate)-dominated pollution characteristics for a few hours during the daytime until the early evening (Table IX and Figure 13), over a longer term of reference (24 h or seven days), the average pollution is definitely domestic-dominated.

There appears to be no obvious differences between weekday and weekend samples for either the Avonside or Woolston sites (Table XII)($\log_{10}$([PAH]/[Pb]) = 1.3661,

1.4545 (Avonside) and 0.9407,1.0889 (Woolston) for weekday and weekend samples respectively). These figures reaffirm the pollution sources dominant (i.e. domestic and mixed, respectively) at these sites.

Low-level pollution samples (< 100 $\mu g/m^3$ APM) from Bealey Avenue tend to give $\log_{10}([PAH]/[Pb])$ values (0.9887 and 0.7835 from Table XIII) suggestive of a more traffic-dominated nature than samples of > 100 $\mu g/m^3$ APM. A result like this is consistent with a roughly constant traffic pollution level being pushed to more elevated levels on colder days or during the night (when usage of domestic fires increases) by the increase in domestic emissions. A similar explanation is applicable for low-level Manchester Street samples (also Table XIII) whose $\log_{10}([PAH]/[Pb])$ values (0.5371, 0.4275 and 0.3393) are well below the lower traffic-zone given in Figure 13. Such a pattern was also observed for the other low-level (seven-day and hourly) samples from the same site.

2.3.4 Atmospheric mixing

During the period when the pollution in Christchurch is at its worse - when stable weather conditions prevail from early evening to mid-morning the following day - the major proportion of the PAH load would be from domestic fires. There will be some atmospheric mixing even under such temperature inversion conditions as described in Section 2.3.1, and it is conceivable that this mixing is responsible for the absence of major differences in PAH

gas chromatographic profiles for Manchester Street, Avonside and Bealey Avenue 24-h APM samples (see Section 2.2.2). In other words, the average (i.e. daily) pollution in most areas of Christchurch during winter is caused by domestic emissions. Specifically, it is this extra load from these sources which mixes with and pushes up the constant PAH level due to traffic sources at localized sites like Manchester Street, that accounts for the similarity of the gas chromatographic profiles.

It is interesting that if variance ratios (F values) are calculated using $\log_{10}([PAH]/[Pb])$ values for combinations of samples from Manchester Street, Avonside, automobile exhaust and CPB (Table XIX, Appendix B), the following observations can be made:

(i) Automobile exhaust and CPB samples cannot be distinguished from each other (as was discussed earlier, in Section 2.3.2).

(ii) The discrimination between exhaust (and CPB samples) and domestic soot samples are highly significant, therefore justifying the use of $\log_{10}([PAH]/[Pb])$ data as sensitive source indicators. This result was previously presented graphically (Figure 12).

(iii) The variance ratio for Manchester Street and CPB samples shows that these two groups of data sets are significantly different, even though both are traffic-dominated. This result is not unexpected, however; rather it agrees with the observation made earlier of the phenomenon of atmospheric mixing which gives rise to the similarities of

the gas chromatographic profiles of Manchester Street and domestic soot samples.

(iv) The variance ratio of Avonside/domestic soot samples only just attains the 1 percent significance level. Ideally, these two groups of samples should not be significantly different from each other. That they are, slightly, can again be attributed to atmospheric mixing which contributes to the lead levels at the Avonside site. The latter in turn manifests $\log_{10}$([PAH]/[Pb]) values which are generally lower than those of domestic soot, a situation depicted in Figure 12.

These results all show that the general average Christchurch atmospheric pollution in winter is principally dominated by domestic fire emissions; nevertheless, the use of $\log_{10}$([PAH]/[Pb]) values can effectively distinguish the sites burdened with localized traffic or mixed-source emissions from the overall domestic-dominated pollution.

2.3.5 Other relationships as source indicators

Having shown that [PAH]/[Pb] ratios are discriminating and sensitive source indicators of PAH emissions, an attempt was made to incorporate other possible variables which, when considered together with [PAH]/[Pb] ratios, would display better discrimination between sampling sites. The [BaP]/[BPe] relationship appeared to be the logical choice, since it has been shown earlier that it can provide reasonable discrimination, notwithstanding the doubtful stability of BaP. Two-variable analyses were carried out on log([PAH]/[Pb]):[BaP]/[BPe],

log ([PAH]/[Pb]):log([BaP]/[BPe]) and [PAH]/[Pb]:[BaP]/[BPe]. Although the 1 percent significance level could be attained by F values computed for all these relationships for Manchester Street/Avonside and Manchester Street/Bealey Avenue samples, Avonside/Bealey Avenue samples were generally significantly different only at the 5 or 10 percent levels, (see Table XVIII, Appendix B). The [PAH]/[Pb] ratio is therefore the most effective means of PAH source identification.

2.4 DETERMINATION OF PAH IN MUD AND BIVALVES

2.4.1 General considerations

While most of the reported studies on PAH in the environment have been conducted on these compounds adsorbed on airborne particulate matter, perhaps because of their potentially more direct and immediate effects on health, in recent years increasing attention has been focussed on other environmental substrates on which PAH may be found. In particular, there has been much interest in the PAH content of the lithosphere. Soils,[16,149] and sediments from the marine,[16,95,149-152] lake,[27,90,99,153,154] river[80,99] and estuarine[155,156] environments have all been analysed for PAH. The composition and distribution of PAH in these materials have been used as a basis for speculation about PAH origins, whether anthropogenic (combustion of fossil fuels) or natural (including natural fires and biosynthesis). Further, information on their chronological depositions[27,90,153] has also been obtained

from the determinations of these compounds in cored sediments.

The determination of PAH in mud in the two Christchurch rivers - the Avon and the Heathcote - and in their common estuary was undertaken as an extension of the general study of atmospheric pollution in the city by this particular class of compounds. (The term "mud" will be used in place of "sediment". It is considered to be more appropriate in view of the fact that most of the sediment samples collected were of the type which dries to a hard mass. Preliminary studies in this work showed that both the "mud" and the true "sediments" (which dry to a friable mass) collected at the same site when both types were present, contain the same levels of PAH.)

From Figure 14, it may be seen that almost the entire lengths of the Avon and Heathcote Rivers run within the Christchurch urban area. The sampling site considered as the Heathcote source (Site A, see Figure 15) is in open farmland and flows for about 200 m through similar country. After that, it continues towards the estuary through urban

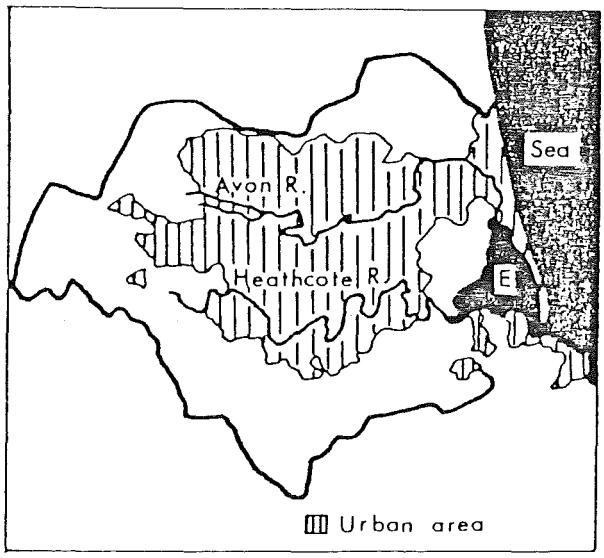


Figure 14. The Avon and Heathcote Rivers and their Estuary (E).

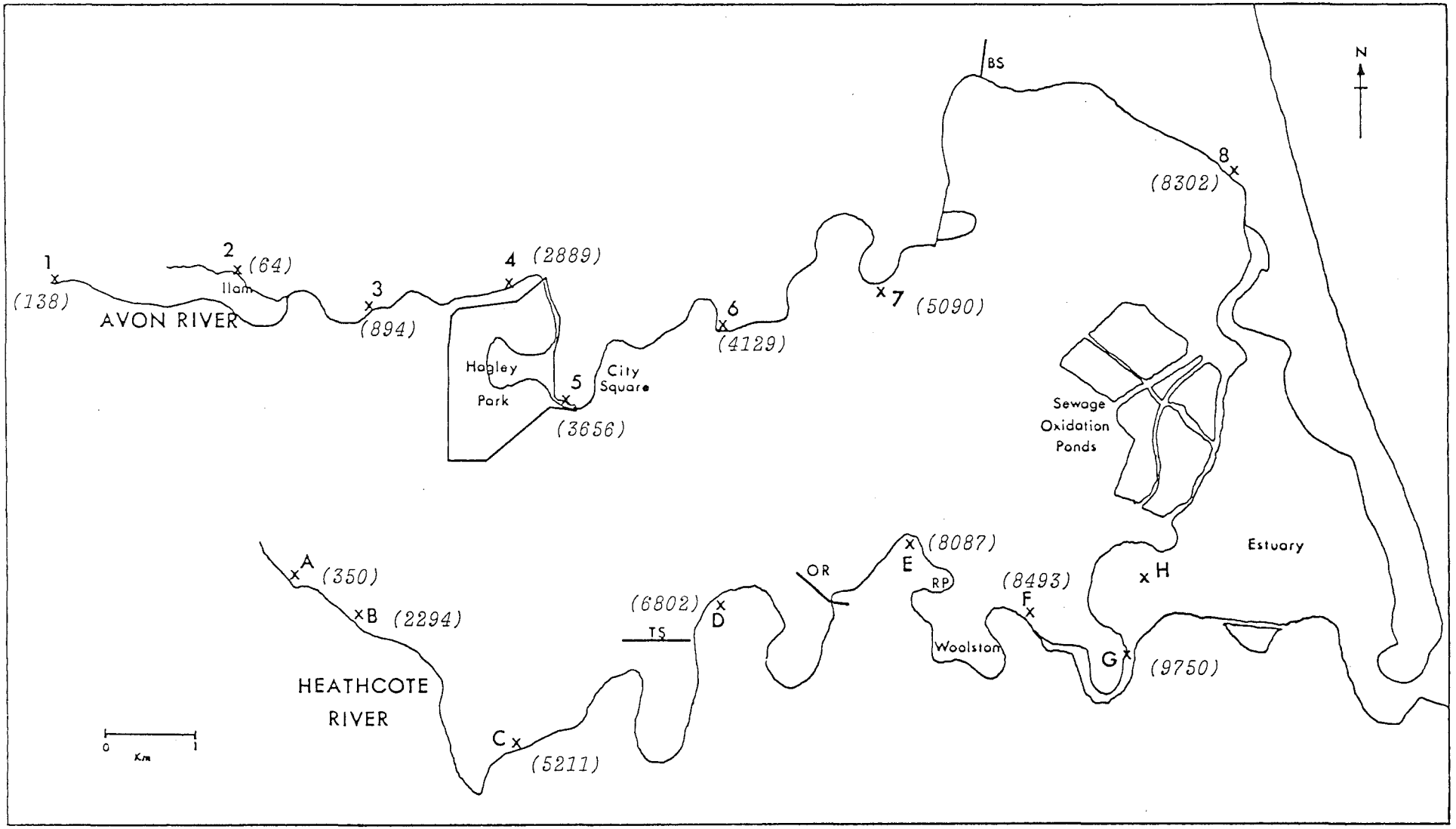


Figure 15. Sampling sites for mud from the Avon (1-8) and Heathcote (A-H) Rivers. Fuller details are given in the Experimental Section. Total (cumulative) catchment area (hectares) contributing to each sampling site is shown in italics.

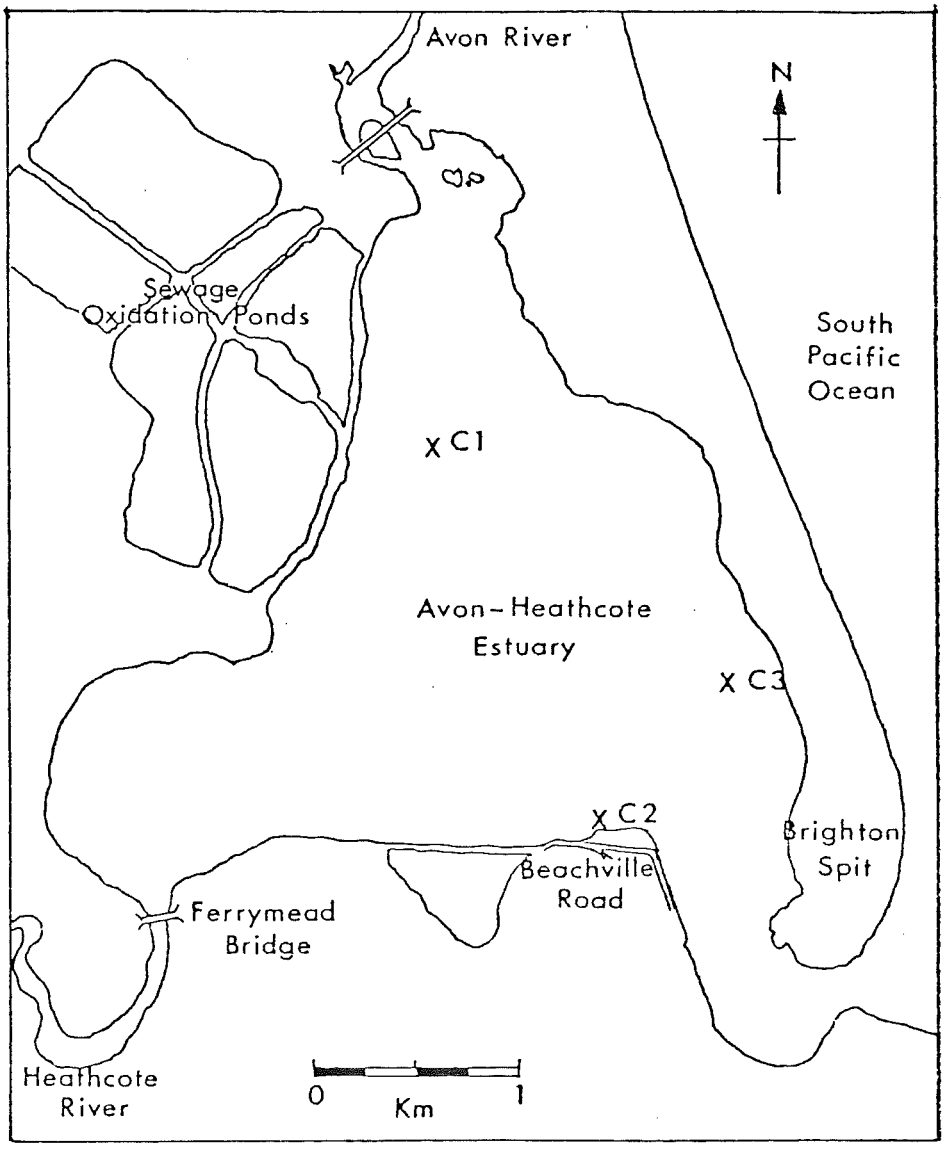


Figure 16. Sampling sites (C1 - C3) for mud and Chione Stutchburyi in the Avon-Heathcote estuary. Fuller details are given in the Experimental Section.

areas. The Avon source (Site 1) is in a lightly residential area (Avonhead) and throughout its course is bordered by well built-up urban areas; the river in fact almost cleanly bisects Christchurch city in a general west-east direction. Being the sinks of a heavily urbanized catchment basin, the two rivers are burdened with a considerable pollution load. One aspect of this study was to determine the distribution of PAH in the mud along the rivers and in their estuary, and thus try and explain the origins of these PAH. As a supplementary exercise, specimens of the bivalve, Chione stutchburyi (the common cockle) collected in the estuary were also analysed. Marine organisms are, of course, often used as monitors of PAH pollution because it is known that they accumulate these compounds in the tissues. Dunn and Young[157] have shown that the ambient level of benzo[a]pyrene in the bivalve, Mytilus edulis (the common mussel) is zero or nearly so, and that any uptake of this pollutant must have been derived from the surroundings. Chione stutchburyi, a mud-dweller, occurs in great abundance (density of $> 2500/m^3$)[158] in the Avon-Heathcote estuary, and therefore seems to be an ideal and convenient subject for assessing the relationship between organism and environment as far as PAH levels are concerned.

Figure 15 shows the sites on the Avon and Heathcote rivers from which mud samples were collected, and Figure 16 the sampling sites for the estuarine mud and Chione stutchburyi specimens.

Levels of PAH determined in mud and bivalves from the sites shown in Figures 15 and 16 are given in Tables XIV, XV

Table XIV. PAH and Pb Concentrations in Heathcote River Mud

	Site	A.Source	B.Spreydon Domain	C.Cracroft Bdge	D.Waltham Rd. Bdge.	E.Radley St. Bdge.	F.Tunnel Rd. Bdge.	G.Ferrymead Bdge.	H.Estuary
	PAH(ppb,dry wt.)	763	2553	5838	7014	40317	17000	6057	3584
	Pb(ppm,dry wt.)	59	94	72	91	382	193	63	41
Peak No.*	Individual PAH (ppb,dry wt.)								
1	BaA	35	164	225	417	2023	796	272	85
2	Chr	51	295	307	597	3361	1667	327	185
3	BF	75	367	976	1240	5241	2589	833	499
4	BeP	59	151	348	517	2388	1006	433	178
5	BaP	77	302	656	709	4080	1560	651	237
6	Pe	29	58	169	201	1327	392	190	79
7	MeBF,MeBP	18	40	122	96	884	305	127	63
8	MeBF,MeBP	23	69	198	128	1493	560	185	63
9	MeBF,MeBP	17	28	90	81	884	259	139	31
10	MethBeP	15	69	118	62	1216	339	137	41
12	DBajA	40	56	148	216	1036	491	190	68
13	IP	63	167	319	527	2051	1184	519	208
14	BPe	72	239	413	563	2720	1242	525	234
15	An	16	271	112	207	1142	509	159	89
16	MeBPe,etc.	6	21	23	40	144	102	29	27
17	MeDBA	21	69	99	92	814	318	108	83
18	MeDBA	5	25	20	41	144	86	28	29
19	MeDBA	5	16	32	49	299	176	30	25
20	MeDBA	4	18	36	69	144	291	12	23
21	DBF	16	77	264	161	608	408	105	121
22	DBF	33	57	316	387	1382	493	203	308
23	DBF,CBPe	28	34	343	278	1659	357	221	222
24	CBPe	16	19	111	128	1277	178	164	194
26	Co	16	5	356	73	863	913	110	387
27	DBP	42	6	116	177	2311	541	229	91
28	DBP	15	34	42	58	826	238	141	14

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 25 (see Table I) were not detected.

Table XV. PAH and Pb Concentrations in Avon River Mud

	Site	1. Source (Norton's Rd.)	2.Okeover Stream	3.Straven Rd.	4.Harper Ave.	5.Antigua St.	6.Fitzgerald Ave.	7.Gloucester St.N.	8.Owles Ter.
	PAH(ppb,dry wt.)	1857	5009	2288	3665	14995	22059	33913	2842
	Pb(ppm,dry wt.)	228	108	85	332	125	117	193	42
Peak No.*	Individual PAH (ppb,dry wt.)								
1	BaA	64	334	150	245	934	1061	1782	167
2	Chr	159	488	276	409	1671	2210	3760	340
3	BF	234	884	446	657	2145	3915	5889	615
4	BeP	85	355	142	242	1114	1772	2672	182
5	BaP	128	595	177	392	1361	2066	3319	287
6	Pe	32	108	48	123	412	495	928	83
7	MeBF,MeBP	25	42	43	64	103	360	668	48
8	MeBF,MeBP	33	91	55	94	309	587	997	58
9	MeBF,MeBP	19	37	29	62	96	299	606	38
10	MethBeP	18	90	36	62	199	288	624	56
12	DBajA	42	140	63	109	377	577	891	65
13	IP	115	347	163	336	1382	2028	2969	180
14	BPe	149	317	185	306	947	1551	2153	223
15	An	46	123	89	104	377	541	866	70
16	MeBPe,etc.	22	37	26	25	43	134	75	17
17	MeDBA	57	135	42	82	1360	379	347	48
18	MeDBA	30	33	13	22	43	170	99	45
19	MeDBA	43	55	20	37	71	186	124	13
20	MeDAB	32	27	20	44	77	155	171	13
21	DBF	110	98	46	37	172	227	495	32
22	DBF	139	143	68	118	463	669	1420	82
23	DBF,CBPe	111	252	54	100	514	834	1208	68
24	CBPe	84	75	31	52	257	482	643	38
26	Co	11	33	14	37	97	180	260	24
27	DBP	46	125	40	102	386	696	836	48
28	DBP	23	45	12	24	86	197	110	2

See Table I for an explanation of abbreviations

*PAH corresponding to peak nos. 11 and 25 (see Table I) were not detected.

Table XVI. PAH and Pb Concentrations in Estuary Mud and Chione Stutchburyi

	Site	C1.Near oxid. ponds		C2.Beachville Rd		C3.End Plover St	
		Mud	Chione	Mud	Chione	Mud	Chione
	PAH(ppb,dry wt.)	1312	671	1985	325	163	108
	Pb(ppm,dry wt.)	41	15	19	10	14	8
Peak No.*	Individual PAH (ppb,dry wt.)						
1	BaA	60	51	93	14	9	-
2	Chr	129	123	191	46	17	-
3	BF	279	145	351	52	23	-
4	BeP	98	67	122	25	20	-
5	BaP	100	98	194	80	25	-
6	Pe	33	15	51	8	1	-
7	MeBF,MeBP	24	11	38	2	trace	-
8	MeBF,MeBP	11	7	33	3	"	-
9	MeBF,MeBP	11	5	25	2	"	-
10	MethBeP	12	7	33	6	"	-
12	DBajA	37	15	45	6	4	9
13	IP	89	49	198	26	36	33
14	BPe	124	69	149	44	24	6
15	An	15	9	22	11	4	55
16	MeBPe, etc.	13	trace	9	-	-	5
17	MeDBA	62	"	90	-	-	-
18	MeDBA	22	"	51	-	-	-
19	MeDBA	13	"	21	-	-	-
20	MeDBA	6	"	9	-	-	-
21	DBF	17	"	28	-	-	-
22	DBF	32	"	84	-	-	-
23	DBF,CBPe	31	"	51	-	-	-
24	CBPe	12	"	18	-	-	-
26	Co	13	"	21	-	-	-
27	DBP	58	"	51	-	-	-
28	DBP	11	"	7	-	-	-

See Table I for an explanation of abbreviations

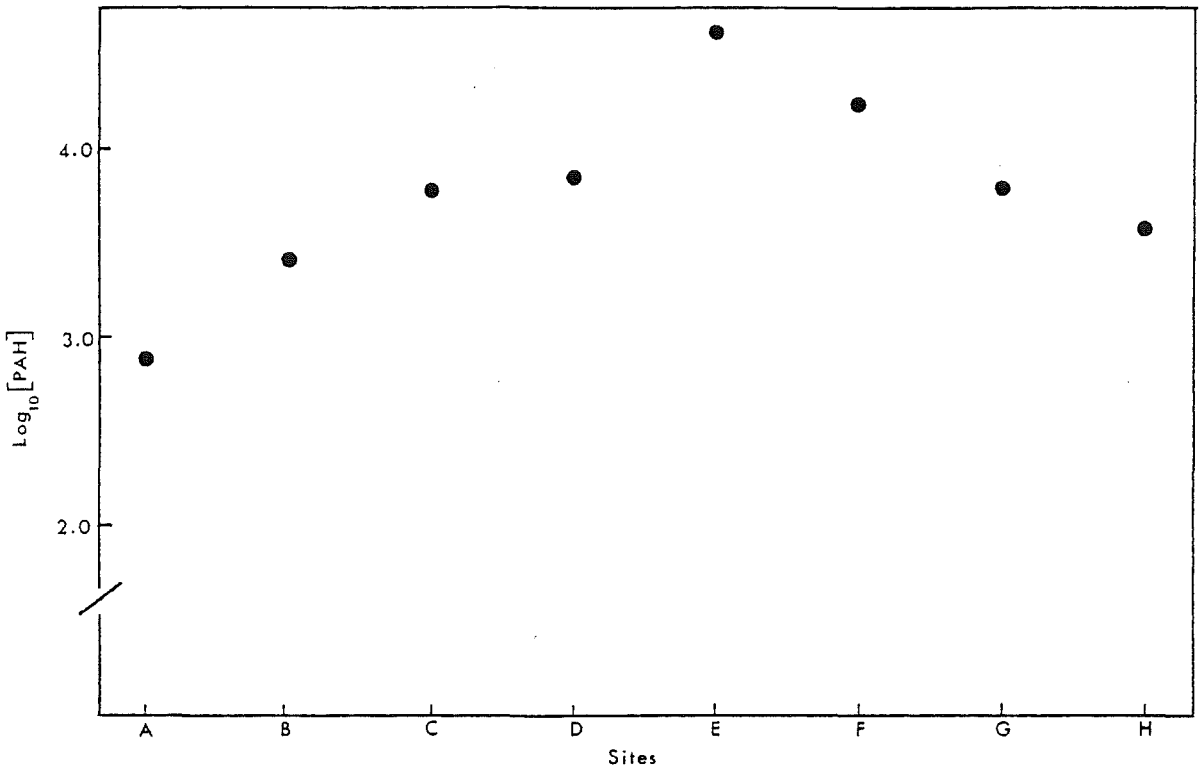
* PAH corresponding to peak nos. 11 and 25 (see Table I) were not detected in all samples.

and XVI which also list the lead levels quantified for each sample. A gas chromatogram of PAH in a mud sample has earlier been presented (Figure 6, Section 2.2.1). All mud samples show similar gas chromatographic profiles.

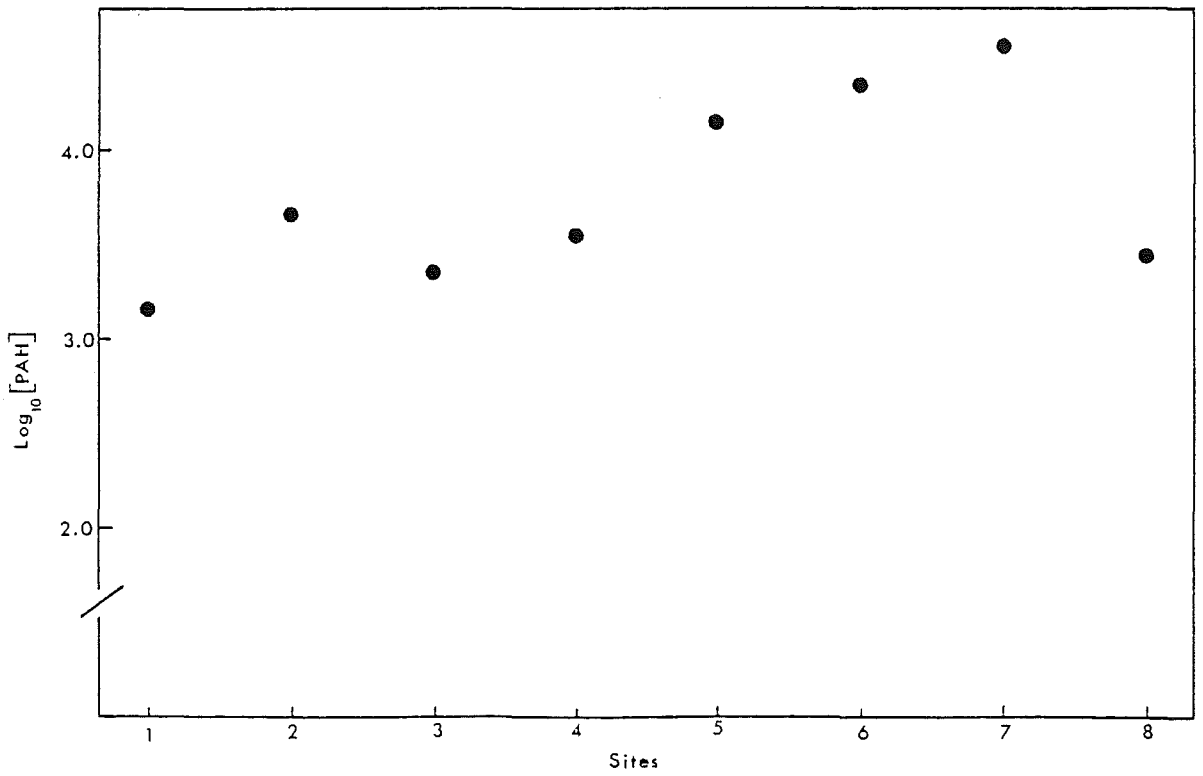
2.4.2 PAH in river mud

Generally, the PAH detected in mud samples from all sites are the same as those which were found to be present on APM. Comparison of PAH gas chromatographic profiles of mud and APM (Figures 3, 4 and 6, Section 2.2.1) reveals that the same PAH are present in both, with minor quantitative differences. Mass spectrometric analysis of the components confirms this observation. As mentioned earlier (Section 2.2.1), the dibenzofluoranthenes (peaks 21 and 22) which are fairly abundant in APM, are only minor components in mud. In addition, cyclopenta[cd]pyrene is not detected, and coronene is present in relatively low concentrations. It is perhaps not surprising that the most volatile components, fluoranthene and pyrene (peaks 29 and 30), occur in great quantities in relation to the other components in mud, since APM sampling by air filtration leads to losses of the volatile PAH if the sampling period is of considerable length (e.g. loss of 78 percent of fluoranthene has been reported for a 12-week collection period[112]).

The distribution profiles of the total PAH levels in mud for the Avon and Heathcote Rivers from source to estuary are shown in Figure 17 (note the logarithmic scale on the vertical axis). Both profiles are similar, each with a



(a) Heathcote River.



(b) Avon River.

Figure 17. Distribution of total PAH in the Heathcote and Avon Rivers. Note logarithmic scale on the vertical axis.

relatively low PAH level at the source building up to a maximum and then falling away again as the estuary is neared. The PAH levels in estuary mud (Table XVI) are higher than those at the sources of the two rivers but are otherwise lower than the values for the other sites.

(a) Heathcote River

The comparatively low level of PAH observed at the source of the Heathcote River (Table XIV) is not unexpected since it is in open farmland. As this river flows through an increasingly urbanized area, there is a rise in PAH levels at each site downstream of the previous site (see Figure 17a). The maximum level recorded (at Site E, Radley Street bridge) - 40317 ppb - coincides with the river entering the Woolston industrial area. For more than 100 years now this district has been the scene of intensive industrial activity, and only in 1972 when the industrial sewer for the area began operation, has the large-scale discharge of industrial wastes directly into the Heathcote River ceased.[160] A 1978 study[160] concluded that the overall quality of the water is very good along this area. Even so, this stretch of the river bank is generally devoid of vegetation and an obnoxious odour is evident in the vicinity. The area supports industries like rubber mills, gelatine and glue works, tanneries, battery manufacturing and engineering works. Given the presence of industrial activities and the general observed condition of the river in this region, it is surprising that as the river flows through it, the PAH level decreases and continues to do so further downstream. The reason for this observation

is not immediately apparent. Between Sites E and F particularly, the PAH level would have been expected to increase if it is accepted that the level at a particular site results from the accumulation of PAH-occluded mud particles due to resedimentation of these particles arriving from further upstream,[152] and also from continual input from the bank up to that site. Initially it was believed that dredging operations (a flood-control measure) might have been responsible for this apparently anomalous observation, but the Radley Street bridge area to the Tunnel Road bridge (Site F) area has not been dredged since 1973.[159] In any case, even if dredging had been undertaken more recently than that both sites should have been equally affected. (Dredging operations along other parts of the Heathcote River affected only Site D, and this was in February, 1975.[159])

Examination of the particle-size composition of the mud/sediments at the respective sampling sites[161] reveals no apparent correlation with the trend of the PAH levels observed. Neither is there any observable relationship between the PAH levels and the organic fraction (determined by loss of weight on ignition at 600°C after drying at 105°C to constant weight[161]) of the mud/sediments, or the rate of water flow (L/s).[161] These parameters therefore cannot account for the decrease in PAH levels in going from Sites E to F (and thereafter).

The increase in PAH levels down the Heathcote River as the total (cumulative) catchment area (see Figure 15) increases, up to a maximum level at Site E, is completely consistent with the increasing run-off and stormwater

catchment area as the river flows towards the estuary. It is impossible to put any sort of quantitative measure of pollutant input from each catchment, apart from area, since the proportion of urbanization of the catchments varies. Additionally, there is no information about the rate at which particulate matter is washed into the river so that the relationship between a catchment area and the sampling site most appropriate to it is not known. As already mentioned, however, the course of the Heathcote lies entirely within the confines of the built-up areas; it follows that the continual input from these areas within each catchment area may explain the increasing PAH levels observed.

The reason for the fall-off in PAH levels towards the estuary (after Site E) is not clear. A possible explanation for this observation might be the release of PAH occluded in mud particles into solution under conditions of vigorous water agitation.[162] However, this possibility was discounted because the stretch of the Heathcote River concerned is not subject to significant water turbulence.[159] Another contributory factor may be that the catchment areas become less urbanized towards the estuary. Also, it seems likely that since the maximum PAH level occurs at about the upper limit (Radley Park, RP in Figure 15) of salinity effects,[159] tidal movements must play some role. Exactly what role is not clear, but two factors must be considered. Firstly, during a large part of the tidal cycle, river flow is reduced, or sometimes reversed (at Opawa Road,[159] OR), so that the amount of sedimentation in these tidal areas may increase (with the concomitant increase in PAH levels).

Secondly, however, the dilution and washing effect of the tides will reduce the particulate deposition. It would appear from the results obtained that the second factor predominates, and is responsible for the decrease in PAH levels observed after Site E.

Yet another possible factor leading to PAH losses from the mud near the estuary is photodegradation. Since samples from all sites were collected near the bank at low tide (see Experimental Section), the mud will have been exposed to light for a few hours each day, an event which could enhance the loss of PAH by photochemical means. This is especially so near the lower reaches of the river where exposure of the mud occurs to a greater extent due to the more considerable tidal influence. Site F, for example has an average tide range of 1.5 m.[160]

(b) Avon River

The source of the Avon River shows a higher level of PAH (Table XV) than the Heathcote but this is explained by the fact that the former is in a residential area. As with the Heathcote River, there is a sharp drop in the PAH level after the maximum (33913 ppb) has been reached at the Gloucester Street North (Dallington) bridge (Site 7); see Figure 17b. Again it may be of significance that Site 8 (Owles Terrace), downstream of Site 7, is in the tidal region of the river (tidal influence penetrates into the Fitzgerald Avenue (Site 6) area and salinity effects are observed above Bassett Street,[159] BS in Figure 15). A PAH dilution effect is very much in evidence in this case as

well. The catchment area associated with Site 8 is largely an uninhabited marsh, unlike the areas contributing at the other sites which are lightly (Sites 1 and 2) to totally urbanized (all other sites). The characteristics (particle-size composition, organic fraction, etc.) of the mud and water flow were also inspected as they were for the Heathcote, and found to have no correlation with the levels of PAH observed.

Except for Site 2 (discussed below) which is a separate tributary of the Avon, all the other sites are on the main river; therefore, like the Heathcote, the catchment area is cumulative for each site downstream of the preceding one (Figure 15). The trend of increasing PAH levels up to the Gloucester Street North bridge can thus be explained in the same way as the trend for the Heathcote.

Site 2 (Figure 15) is actually on the Okeover Stream, a branch of the Avon, and is not the same one which arises from the source (Site 1). However, these two streams join ca. 500 m downstream of Site 2 to form the main Avon River. The catchment areas contributing at Sampling Sites 1 and 2 are therefore distinct from each other; the area associated with Site 1 is not drained by the Okeover Stream. The catchment area for Site 2 (64 ha) is smaller than the areas for Sites 1 (138 ha), 3 (894 ha) and 4 (2889 ha),[159] yet it shows a higher PAH level (5009 ppb) than each of these sites (1857, 2288 and 3665 ppb respectively).

Site 2 is less than 100 m away from the 50-m high smoke stack of the boiler house of the University of Canterbury. Pulverized coal is used for the boiler, and the outfall from

the smoke stack over the vicinity could explain the elevated level of PAH observed at this site. The catchment area of the Okeover Stream consists of almost equal proportions of open country and urbanized areas,[159] and while urban waste waters will contribute to the overall PAH load at Site 2, the proximity of the boiler house suggests that much of the PAH content originates from the smoke stack, i.e. emissions from coal combustion. The high PAH level at this site certainly supports this view.

2.4.3 PAH in estuarine mud and Chione stutchburyi

In general, PAH levels in estuarine mud are lower than any of those in river mud except at the sources. It thus appears that the conditions that prevent the accumulation of PAH in the mud at the lower reaches of the Avon and Heathcote Rivers persist in the estuary as well. The small number of samples collected precludes any detailed discussion about the distribution of PAH levels within this area; however, the trend seems to be that these levels decrease as the sea is approached.

PAH levels in Chione also show a decrease from the oxidation ponds seawards. A previous study[163] of the Chione community in the estuary, undertaken to define the food sources of this organism by using the stable isotopes of carbon as natural tracers, concluded that Chione feeds on organic matter of terrestrial origin at Site C1 and of marine origin at the estuary mouth (i.e. near Sites C2 and C3). Since the PAH content in organic matter of terrestrial origin should be higher than that of marine origin, due to

the heavier pollution load, Cl bivalves should be burdened with a higher level of PAH than the specimens from the other two sites; this result is indeed observed. Again, since only a limited number of Chione sampling sites were considered, the latter conclusion should be treated with caution.

In general, the PAH levels in Chione are lower than those of the corresponding mud samples (Table XVI). That there are PAH present at all suggests that Chione does bioaccumulate these compounds in its tissues. It may be worth recording that Chione specimens collected at Cl are only half as large as those picked from the other two sites.

2.4.4 Lead in mud and Chione stutchburyi

Lead levels in the mud of the Heathcote River and the estuary show the same trend as the PAH distribution, with concentrations decreasing towards the sea after a maximum has been reached at Site E. The values shown in Tables XIV and XVI agree with those determined in previous studies.[140,159] There is more variation in the lead levels in Avon River mud - a pattern not coincident with the PAH levels (Table XV). Nevertheless, the results are also very much in agreement with those obtained previously.[159]

The bioaccumulation of lead in Chione follows a similar distribution as for PAH, with lower levels observed in the tissues than in the surrounding mud.

2.4.5 Sources of PAH found in mud

The [PAH]/[Pb] ratios used successfully to identify sources of PAH emissions into the atmosphere are not likely to be useful for samples from an aquatic environment. This is because the pollutant-substrate relationships for airborne PAH and lead which are similar for atmospheric samples (i.e. PAH and lead are both associated with similarly-sized atmospheric particles), cannot be assumed to be the same in mud. Differences in solubility in water of individual PAH may also result in a change of the original distribution of PAH from a particular source emitting these compounds into the atmosphere, to a different distribution in the aquatic environment. The use of ratios of individual PAH as a means of source identification is therefore likely to be of little or no value. In addition, it has been reported[164] that the rates of adsorption of different PAH onto solid surfaces in an aqueous medium (in which the PAH were originally dissolved) are different. This again could be reflected in the distribution of PAH in mud being different from that in APM.

Because the water environment is a sink for a wide variety of pollutants including the same types of pollutants from different sources, it is often difficult to attribute the presence of a particular class of contaminants to any one of several possible sources, unless the source is localized and clearly identifiable. For example, elevated lead levels in the mud from a stream flowing in the vicinity of a battery works presumably arise from the effluent discharged from that factory,[140] under normal circumstances.

The same difficulty applies to the problem of determining the sources of PAH in mud. The Avon and Heathcote Rivers, as shown by Figure 14, flow through the Christchurch urban area. Of the many sources which might contribute to the PAH load in the mud of these rivers, perhaps two are predominant - traffic and domestic emissions. It has been shown earlier that the PAH gas chromatographic profiles of all APM samples (regardless of sites) are virtually identical with those of domestic soot samples; this suggests that the bulk of the overall atmospheric pollution for Christchurch is due to domestic emissions. With one minor difference, the gas chromatographic profiles of all the mud samples are the same as those of soot and APM samples; this includes the PAH in mud from the Okeover Stream site (Site 2, Figure 15) which is derived largely from effluent from the smoke stack of the University's coal-fired boiler (Section 2.4.2b). These results support the view that the PAH content of river mud arises mainly from atmospheric PAH pollution, which in turn is mainly of domestic origin. The minor difference between the mud and APM samples is found in the profiles of the compounds corresponding to peaks 21 - 25 (dibenzo-fluoranthenes and cyclopentabenzo[ghi]perylenes); this could arise from solubility or stability differences in this group of PAH.

Qualitative comparisons of PAH gas chromatographic profiles have been used[16] to identify PAH sources in river and marine sediments in spite of the inherent difficulties of such an approach. In this study, the mud profiles are clearly different from those for car park building APM or

exhaust samples - the same qualitative differences, of course, as observed between APM and automobile-dominated samples (Section 2.2). Since the [PAH]/[Pb] ratio is inapplicable to the mud samples, this can only be cited as further evidence that the mud samples are dominated by domestic pollution.

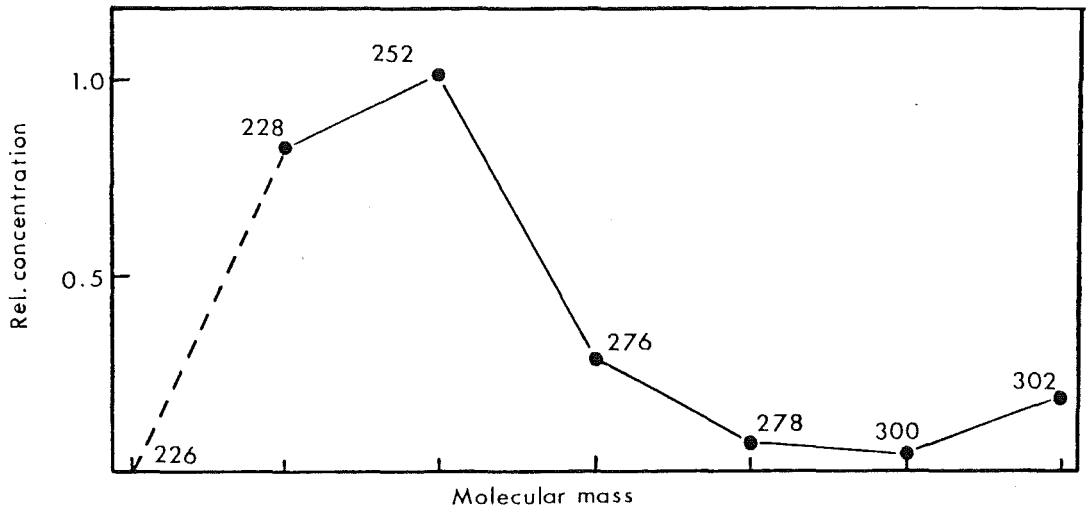
There are various modes of transmission of domestic emissions into the water environment. PAH adsorbed on APM can find their way to the ground by direct settling or through rainfall or snow. Run-off water can then collect this fall-out into rivers, streams and other aquatic systems. In places remote from rivers, etc., run-off water can generally permeate through the soil with its PAH load,[165] ending up as ground water which eventually finds its way into streams and other surface waters. In Christchurch, the situation would seem to be that PAH-adsorbed APM is emitted, principally by domestic fires, into the atmosphere. Some of these air-borne particulates settle directly on the water, ground and other surfaces at or near ground level (e.g. rooftop and vegetation). Precipitation will help to deposit much of the rest of the APM on the same surfaces and the subsequent presence of run-off water will remove much of the material, including that deposited earlier, into aquatic systems. Surface-washings due to human activities, of course, will also occur to some extent.

2.4.6 Parent compound distribution

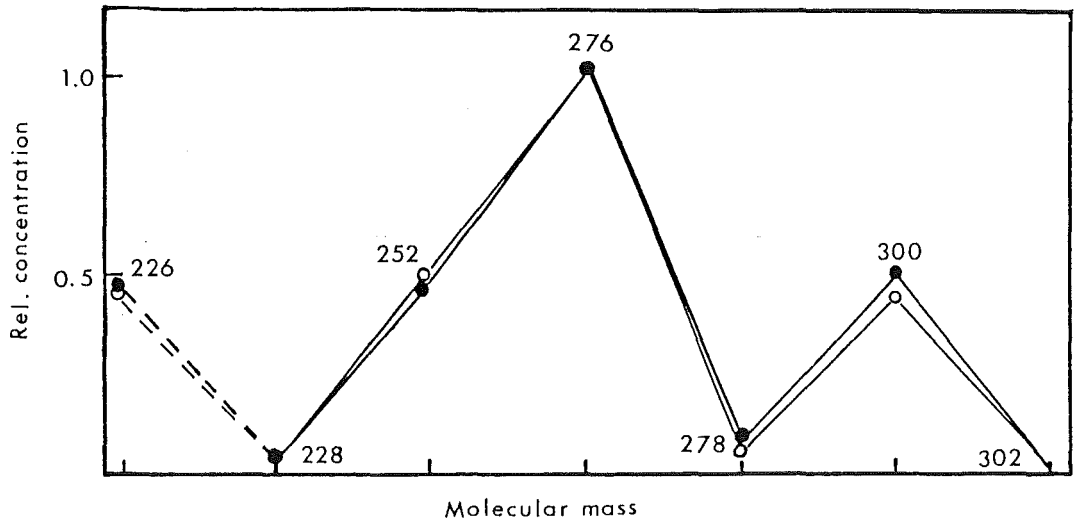
In the time taken for PAH produced by the original sources to be deposited in the aquatic environment, including

mud, there may well have been changes in the distribution patterns of these compounds, possibly due to the reasons already discussed earlier. Nevertheless, one of the techniques that has been used for determining the sources of PAH in sediments (mud)[155] (and also APM[166]) is to compare the parent compound distributions (PCD) of known sources to those of sources to be identified. Similarities of such profiles may indicate that the PAH are derived from the same sources. PCD are simply the relative concentrations of the non-alkylated PAH. (A very similar technique, that of comparing alkyl homologue distributions, using alkylated PAH which are determined from their mass spectral ion intensities, has also been used for source identifications of PAH in sediments.[16,49,155]) For this work, PAH of the following molecular masses (Mr) were used to calculate PCD: 228(benz[a]anthracene and chrysene), 252(benzofluoranthenes, benzopyrenes and perylene), 276(indeno[1,2,3-cd]pyrene), benzo[ghi]perylene and anthanthrene), 278 (dibenz[a,j]-anthracene), 300 (cyclopentabenzo[ghi]perylenes and coronene) and 302 (dibenzofluoranthenes and dibenzopyrenes). PCD were calculated by adding the concentrations of the PAH of each of the molecular masses, and then normalizing these concentrations.

The PCD of known sources (i.e. domestic soot, exhaust and car park building (CPB) samples), calculated from the data in Tables VI - VIII (Section 2.3.2) are shown in Figure 18. The broken lines in both (a) and (b) are extrapolations for cyclopenta[cd]pyrene (CYC, Mr 226). It was found by GC-MS (Section 2.2.1) that the soot samples

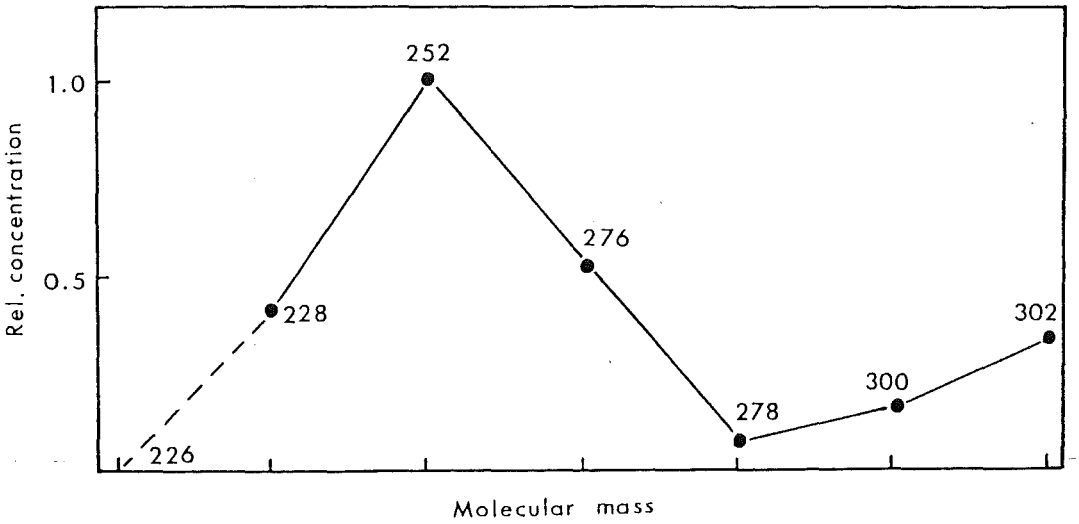


(a) PCD of soot samples

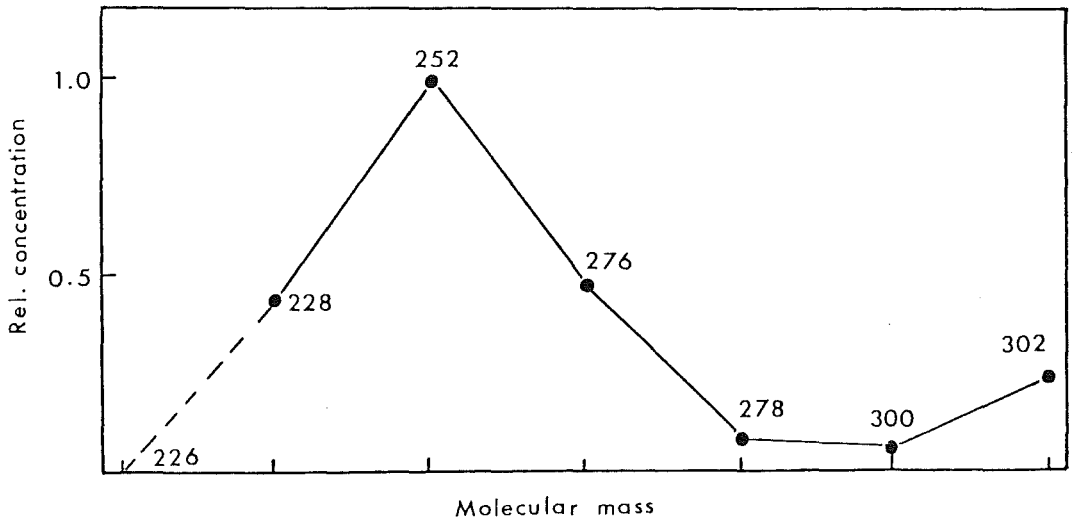


(b) PCD of exhaust (●) and CPB (o) samples

Figure 18. Parent compound distributions (PCD) of soot, exhaust and car park building (CPB) samples.



(a) PCD of Heathcote River mud



(b) PCD of Avon River mud

Figure 19. Parent compound distributions (PCD) of Heathcote and Avon River mud (no CYC detected in both).

contain almost no CYC; thus the relative concentration of this compound should be nearly zero (Figure 18a). On the other hand, exhaust and CPB samples possess large quantities of CYC (which was quantified) and almost negligible amounts of benz[a]anthracene and chrysene (not quantified) - the PCD for these samples thus appear as in Figure 18b. From Figure 18, it is obvious that PCD for soot, and exhaust and CPB samples are different.

If the PCD for mud from the Avon and Heathcote Rivers are calculated (from Tables XIV and XV, Section 2.4.1) and presented in the same way, (Figure 19) the similarity between Figures 19a and 19b with Figure 18a is obvious. This again supports the view that the PAH in mud originate largely from domestic soot emissions. Support for this conclusion comes from the PCD of Manchester Street, Avonside and Bealey Avenue 24-h APM samples (Figure 20), all of which, it has been seen, display strong domestic-dominated pollution. The PCD for these APM samples are identical to those for mud.

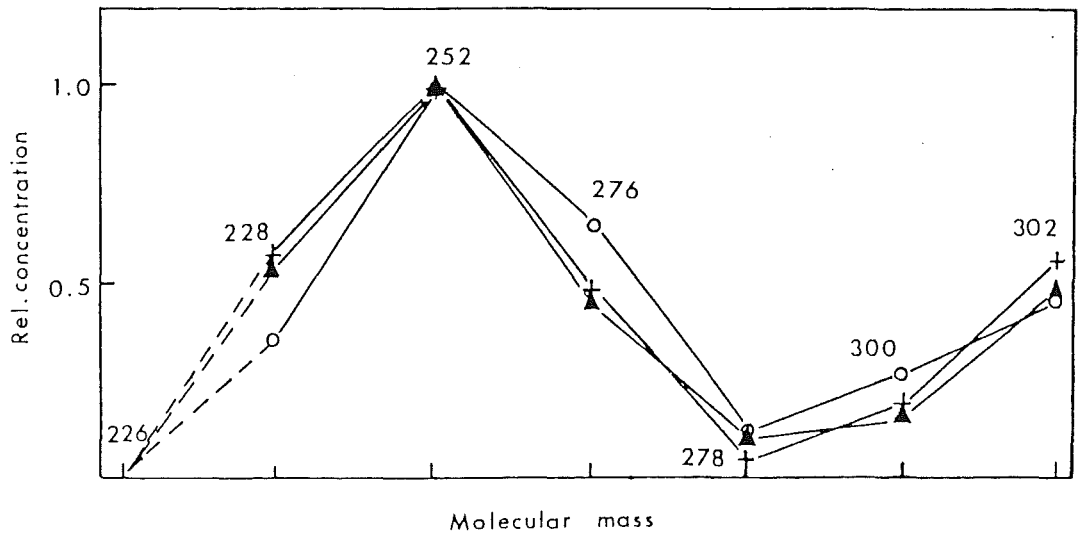


Figure 20. Parent compound distributions (PCD) of Manchester Street (o), Avonside (▲) and Bealey Avenue (+) APM samples.

The PCD for APM samples also support the earlier conclusion based on the similarity of GC profiles, that APM samples can only be differentiated by statistical analysis of the PAH and lead concentrations. It is nonetheless interesting that the PCD of Manchester Street samples show some deviation from those of Avonside and Bealey Avenue - note the points for Mr 276 and 300 (Figure 20), which display an upward shift in the plot. Benzo[ghi]perylene, one of those PAH with Mr 276, and coronene (Mr 300) are, of course, found in relatively greater concentrations in traffic than in domestic soot pollution samples (Section 2.3.1).

2.5 ULTRAVIOLET ABSORPTION STUDIES OF PAH MIXTURES

Whereas the criticism against earlier methods of PAH determination was that only some of the carcinogenic components (usually benzo[a]pyrene) were quantified, the complaint that is generally directed at more recent techniques has been the length of time that a complete analysis requires. Unfortunately, the excellent results normally possible with these techniques are usually dependent on preliminary clean-up operations on environmental samples which, of course, contain a wide variety of compounds other than PAH. The trend in PAH analysis has been to improve the separation of individual compounds because of their different carcinogenic properties; hence the widespread use of capillary columns in gas chromatography (GC). There have also been efforts to reduce or eliminate the clean-up

steps, and high performance liquid chromatography has played an important role in this respect.[42,66]

The results of APM analysis in this work have clearly shown that [PAH]/[Pb] ratios are excellent indicators of PAH source emissions. A logical extension of this study is therefore to develop a method which can be used to determine the total concentration of PAH without the use of GC - the present technique used. Although only the higher molecular mass PAH were considered in this study to reduce the analysis time by GC, it is evident from the description of the sample extraction and clean-up procedures in the Experimental Section that a considerable amount of time is spent in the preparation of a sample for analysis. The following discussion describes the preliminary studies undertaken to develop a method for PAH determination, with emphasis on simplicity of sample clean-up (and therefore on rapidity of analysis). Since all aromatic compounds absorb in the ultraviolet (UV) range, UV absorption was the technique chosen for this purpose. In addition, λ_{max} values for most of the major PAH components are available from the literature.[167]

2.5.1 Beer's Law[168]

Beer's Law expresses the relationship between the amount of light absorbed by a solution and (a) the concentration of the solution and (b) the thickness of the solution through which the light passes.

$$\log_{10} I_o/I = \varepsilon c b$$

I = intensity of the transmitted light

I_o = intensity of the incident beam

ε = molar absorptivity

c = concentration in moles/litre

b = thickness of solution (cm)

$\text{Log}_{10}\ I_o/I$ is known as the absorbance (A), i.e. $A = \varepsilon cb$. b is a constant since the same cell is used throughout and ε is a constant for a compound at a particular wavelength. Thus,

$$A \propto c$$

To show that this relationship holds for a complex PAH mixture, an authentic sample was extracted and cleaned up as described in the Experimental Section, and its absorbances measured at various dilutions on a Varian Super Scan 3 Ultraviolet/Visible Spectrophotometer (Varian Associates, Inc., USA). The measurements were made in cyclohexane. The eluate from the Sephadex LH-20 column (the final clean-up stage) was concentrated down to dryness and the appropriate quantity of cyclohexane added to dissolve the extract for the UV measurements. Since the sample solution was a complex mixture of many PAH, its concentration could not be measured in moles/litre and thus the absorbance measured at a particular dilution had to be expressed in another way as explained below. For convenience, only twelve PAH,* whose λ_{max} values are available were

---

* Benz[a]anthracene, chrysene, benzo[a]pyrene, benzo[e]pyrene, perylene, dibenz[a,j]anthracene, benzo[ghi]perylene, anthanthrene, coronene and the three benzofluoranthenes.

considered. These PAH are also the major components of most types of samples analysed in this work.

For a solution of this sample, the absorbances were measured at all the λ_{max} values (as given in the literature) for each of the twelve PAH. For example, λ_{max} for dibenz[a,j]anthracene are 290, 305, 374 and 385 nm. The absorbances were measured at each of these wavelengths. The sum of all these absorbances together with those of the other eleven PAH were then used to give a term, ΣA at 52 wavelengths (total number of λ_{max} values considered for the twelve PAH). This procedure was then repeated for the sample at various known dilutions. A plot of ΣA against concentration (Figure 20) gives a straight line (correlation coefficient, r = 0.9995) which shows that this complex PAH mixture does obey Beer's Law, which is modified to $\Sigma A = \varepsilon' cb$, where ε' is the general molar absorptivity for the λ_{max} values from which ΣA is measured.

2.5.2 The ΣA vs. c (concentration) relationship

A series of samples whose PAH concentrations had been quantified by GC and which had then been stored in sealed tubes, was prepared by first evaporating off the original solvent (dimethylformamide, DMF) and then redissolving the residue in known volumes of cyclohexane. These samples had all undergone the complete extraction scheme. The ΣA values were then measured for the twelve PAH, as before. The concentration of each solution had to be expressed in µg/mL (ppm) because of the mixture of compounds in it. By plotting ΣA against concentration, it was hoped that a

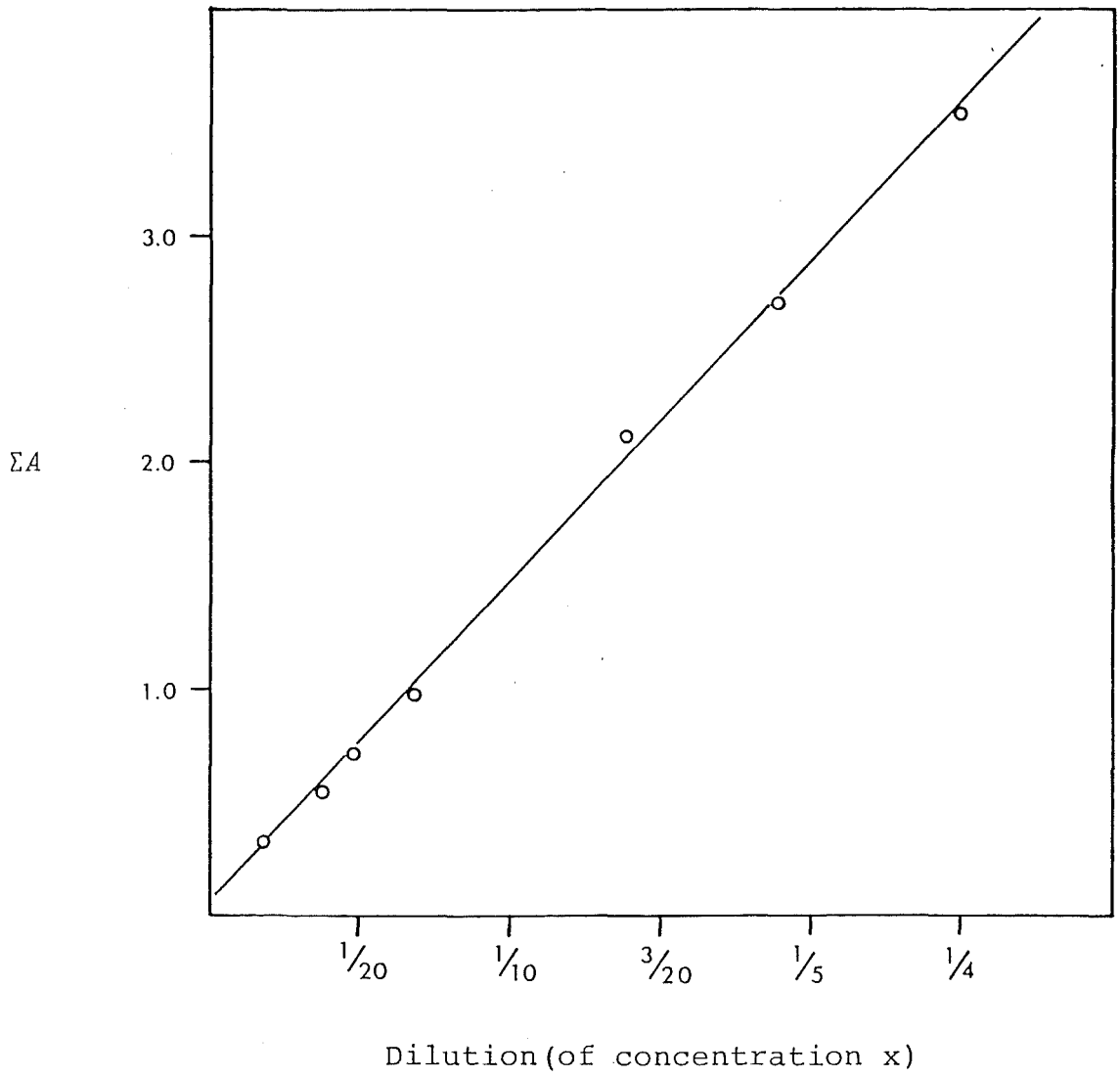


Figure 20. Plot of ΣA vs. concentration of PAH mixtures in cyclohexane solutions.

calibration graph could be obtained so that by measuring the ΣA of a particular sample, its total PAH concentration could be determined from the graph. Unfortunately, such a plot of the results obtained (Figure 21) shows a scatter even though it tends towards a straight line in a form as depicted by Figure 20. The correlation between ΣA and concentration is poor ($r = 0.597$).

It is not surprising that Figure 21 shows considerably more scatter than is considered acceptable in such work. Part of the problem lies in the fact that the dilutions and evaporations leading up to the gas chromatographic analysis were not made quantitatively since these analyses used an internal standard - in particular the volume of solvent (DMF) used to dissolve the Sephadex LH-20 eluate was not measured accurately, and the removal of 2-propanol and DMF could not be made quantitative. Furthermore, the fraction of the total material removed for gas chromatographic analysis was not known exactly, so that the concentration of the final UV solution could not be accurately related to the original amount of PAH. The other factor which might be expected to lead to scatter is variation in the proportions of the major PAH present, since each of these will have different ε values at any given wavelength; in preparing the calibration graph (Figure 20) which demonstrated Beer's Law behaviour, of course, a constant mixture of PAH was used. In spite of the scatter, however, the worst error from the least squares line through the points would give a concentration value of 3 µg/mL. A systematic change in PAH distribution (including that of

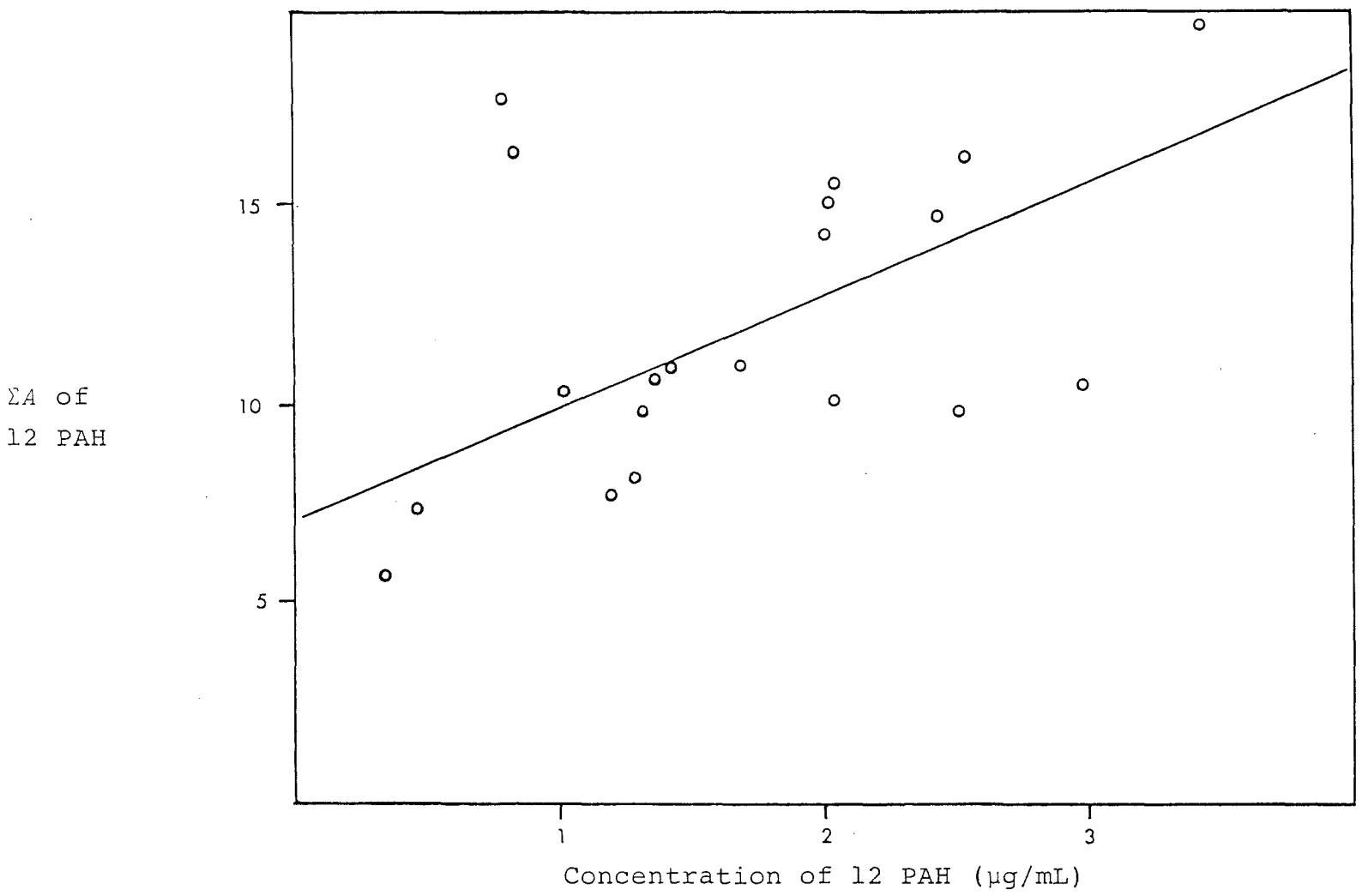


Figure 21. Plot of ΣA against concentration of PAH mixtures from a variety of sources.

components not considered due to lack of information about their λ_{max} values and which therefore could cause variations in absorbance measurements merely by their presence in the UV solutions) from one end of the environmental scale to the other would also lead to scatter, since samples from anywhere in the environmental range may lie anywhere on Figure 21.

As a matter of interest, the modified molar absorptivity, ε', values were calculated for the samples analysed. If it is assumed that ε' is analogous to the normal ε (for one λ_{max}) in that it is an overall value for different λ_{max} values in a complex mixture (52 λ_{max} values were used for the twelve PAH, see above), then for a particular sample,

$$\Sigma A = 52\varepsilon' cb$$

where b = 1 cm. It is also assumed that the "molecular mass" of the PAH mixture is 260 (approx. mean of the molecular masses of the twelve PAH).

Then

$$\varepsilon' = \Sigma A/52 \times 260/wt$$

where wt is the weight (g) of the twelve PAH determined by GC.

Using this result, ε' values were calculated for several samples from various sources (most of them represented in Figure 21), and are listed in Table XVII. Although the values range from 1.2×10^4 to 9.8×10^4, most

Table XVII. Modified Molar Absorptivity (ε') values calculated for various PAH sample solutions (see text)

Sample		ε' (x 10^4)
APM:	1	2.4
	2	3.6
	3	4.3
	4	3.8
CPB:	5	3.2
	6	3.7
	7	3.8
	8	3.3
	9	5.1
	10	1.8
	11	3.6
	12	1.9
Exh:	13	4.3
Mud:	14	8.1
	15	3.1
	16	4.1
	17	3.9
	18	2.9
	19	3.2
Soot:	20	9.8
	21	1.2

of them are reasonably consistent. Again the wide range probably arises from difficulties in measuring the concentration of the twelve PAH. However, the fairly consistent results for most of the samples, even though they were not all from the same source, is encouraging. If an identical value for ε' is obtained for all samples whatever their source, then the concentration of a PAH mixture (containing the twelve components) can be calculated by merely measuring its ΣA value in a known volume of cyclohexane. A constant ε' value would mean that a single calibration graph would be applicable to any sample regardless of the source of the PAH.

As it stands now, no firm conclusions can be made about the feasibility of this method for a rapid determination of PAH mixtures. A larger data base is perhaps required before it can be ascertained whether the modified molar absorptivity (ε') is the same for all samples, and also even with the presence of minor components, the ΣA values are directly proportional to the concentrations of the twelve PAH considered, as Figure 21 appears to show.

Ideally, UV spectra of PAH solutions (after clean-up) should be obtained before the gas chromatographic quantification. In this way, the transfer of solutions is kept to the minimum for the UV analysis, and errors involving the PAH concentrations can be eliminated. The present studies were conducted after gas chromatographic determination had been carried out and the samples stored in sealed tubes for some considerable time, and for reasons already discussed, substantial errors had been expected in the PAH concentrations

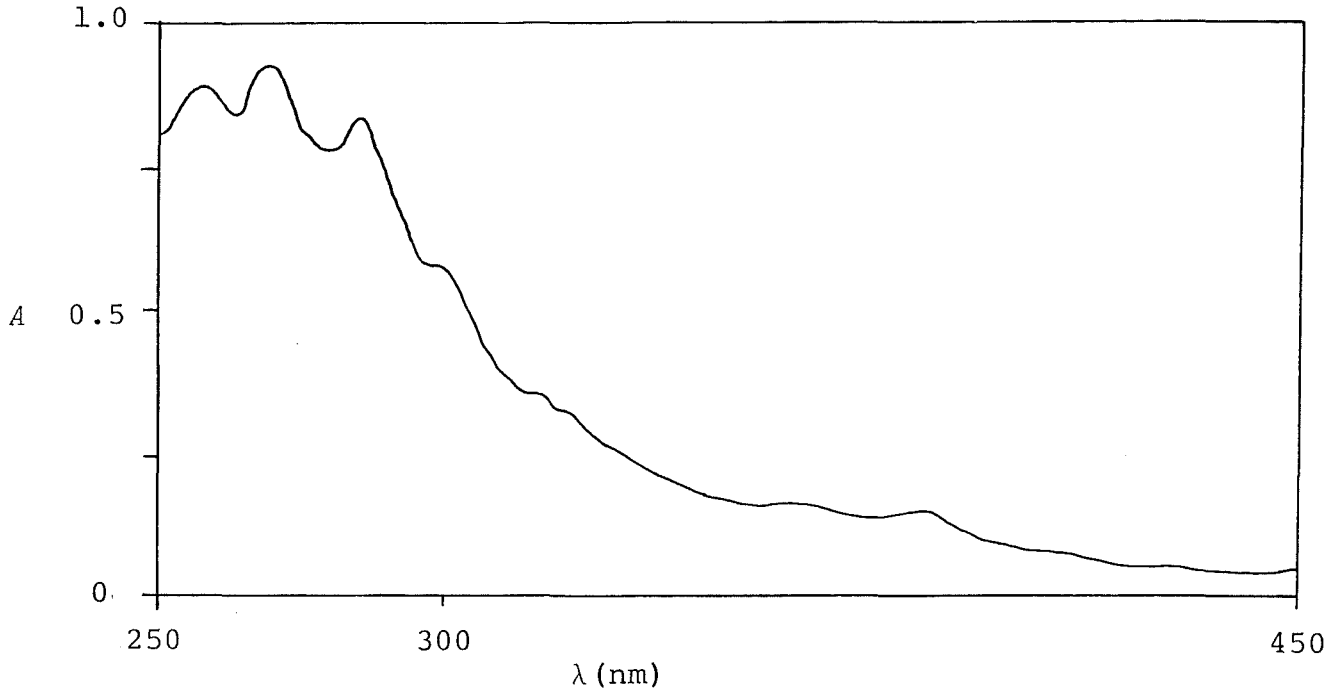
of the solutions used for UV measurements. It is felt that it is these uncertainties that are responsible for the scatter in Figure 21.

In summary then, this investigation, although it dealt with only a limited number of samples, has shown that the quantitative UV absorption method just described may well be satisfactory. There is no doubt about the validity of Figure 20 and the results obtained in the preliminary study on authentic samples from various PAH sources appear promising.

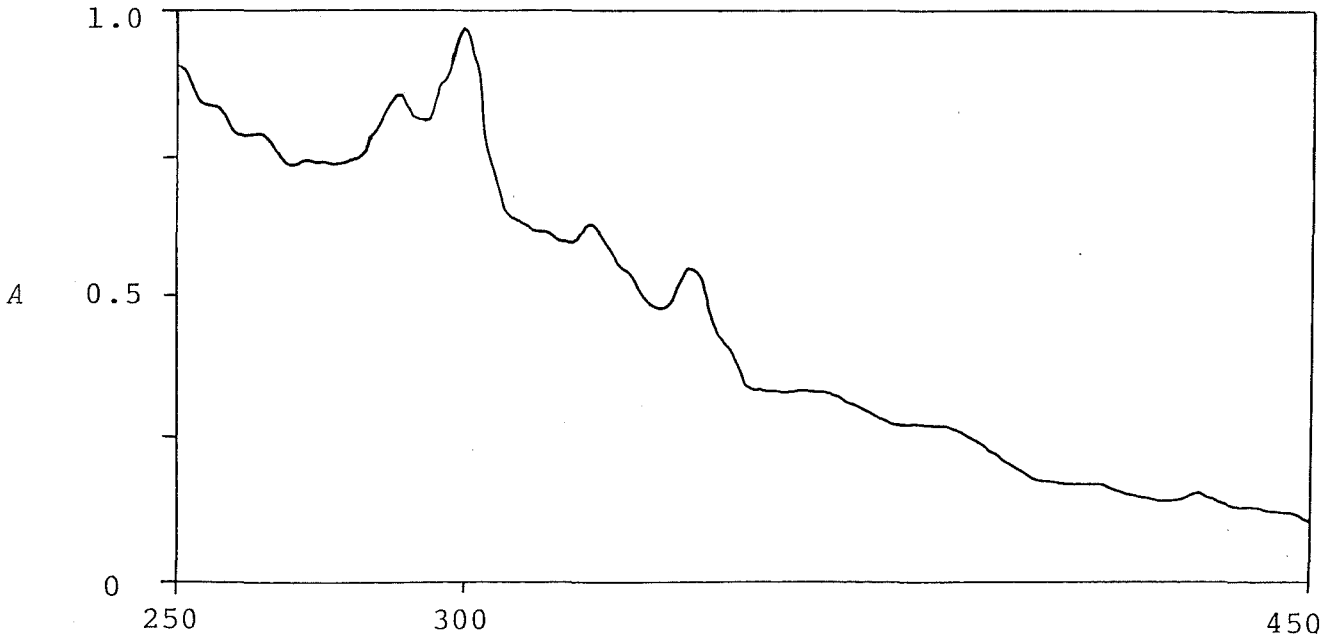
2.5.3 UV absorption spectra of PAH mixtures

Concurrent with the UV studies just described, there arose the opportunity to consider qualitatively the UV absorption spectra of PAH mixtures derived from the various sources. The majority of the samples used to obtain the UV spectra had been stored in sealed tubes under cold, dark conditions. They were prepared for UV measurement as already described (Section 2.5.2).

Figure 22 shows the UV spectra of a PAH from (a) a domestic soot sample and (b) an automobile exhaust sample, after extraction and clean-up according to the procedure given in the Experimental Section. The two spectra show some obvious differences. While the major absorptions of the soot sample are at ca. 285 nm and below, the exhaust sample absorbs very strongly at ca. 287.5 nm and ca. 300 nm. There are minor absorptions for this latter sample at ca. 322 nm and ca. 337.5 nm. The critical difference, however, appears to be at the wavelength of ca. 300 nm. Domestic



(a)



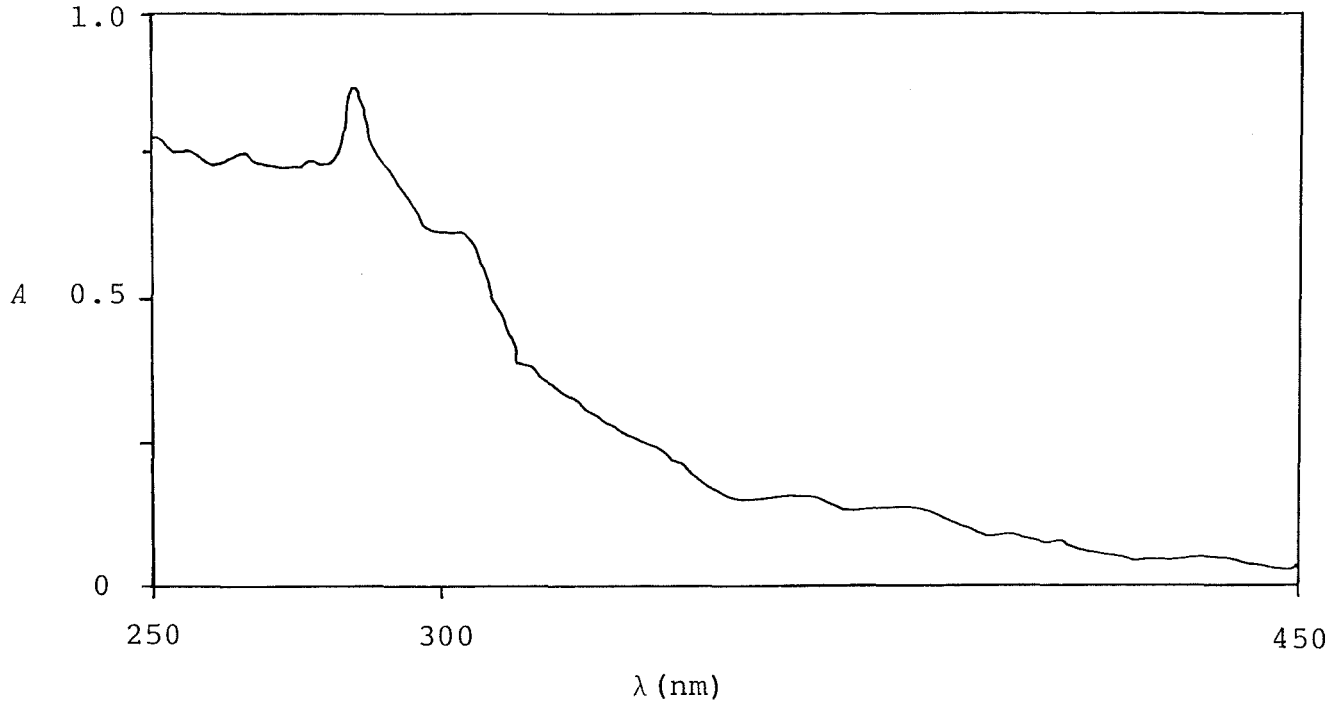
(b)

Figure 22. UV spectra of PAH mixtures from (a) domestic soot and (b) automobile exhaust samples.

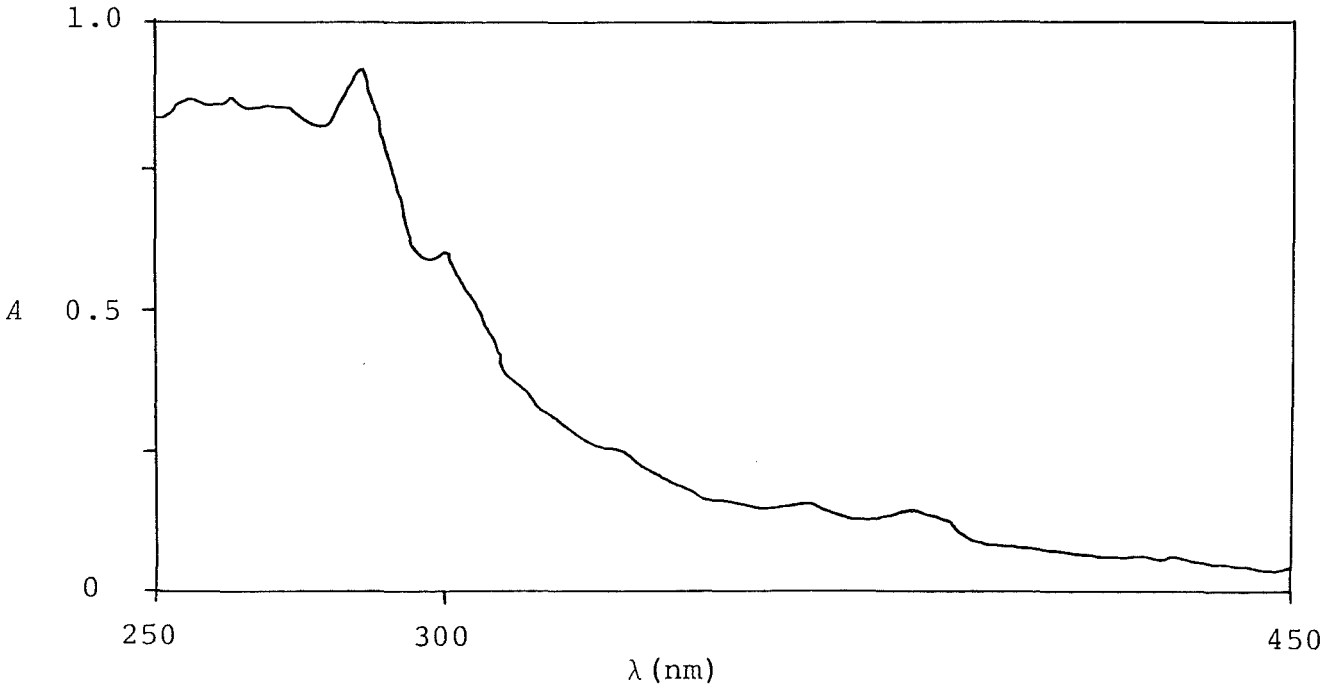
soot samples show no absorption at or around this wavelength, but the maximum absorption for exhaust samples lies in this region, the reason being that benzo[ghi]perylene and coronene, which are major components in exhaust emissions, have λ_{max} values in this region. Another major component of exhaust emissions, cyclopenta[cd]pyrene, is probably responsible for the absorption at ca. 287.5 nm.[169] There are other PAH which absorb around these regions but they are not as abundant as these three.

The above observations suggest that by comparing the UV spectrum of a sample from an unknown source with the two reference spectra (by paying particular attention to the presence or otherwise of an absorption at ca. 300 nm), it may be possible to identify this particular source, on a qualitative basis, at least as a first approximation. Such comparisons were carried out with samples from a variety of sources; the spectra are shown in Figure 23.

The spectra (a) and (b) in Figure 23 both show striking similarities with Figure 22(a), with major absorptions at wavelengths below ca. 285 nm, and these samples were indeed selected from sources dominated by domestic pollution, as ascertained previously (Sections 2.3 and 2.4). The UV spectrum for a Bealey Avenue sample, Figure 23(c), also resembles Figure 22(a); although this area is of mixed traffic-domestic pollution, [PAH]/[Pb] and especially the less discriminating [BaP]/[BPe] ratios have earlier been used to establish that domestic pollution is the stronger component at this site. The same conclusion was also reached

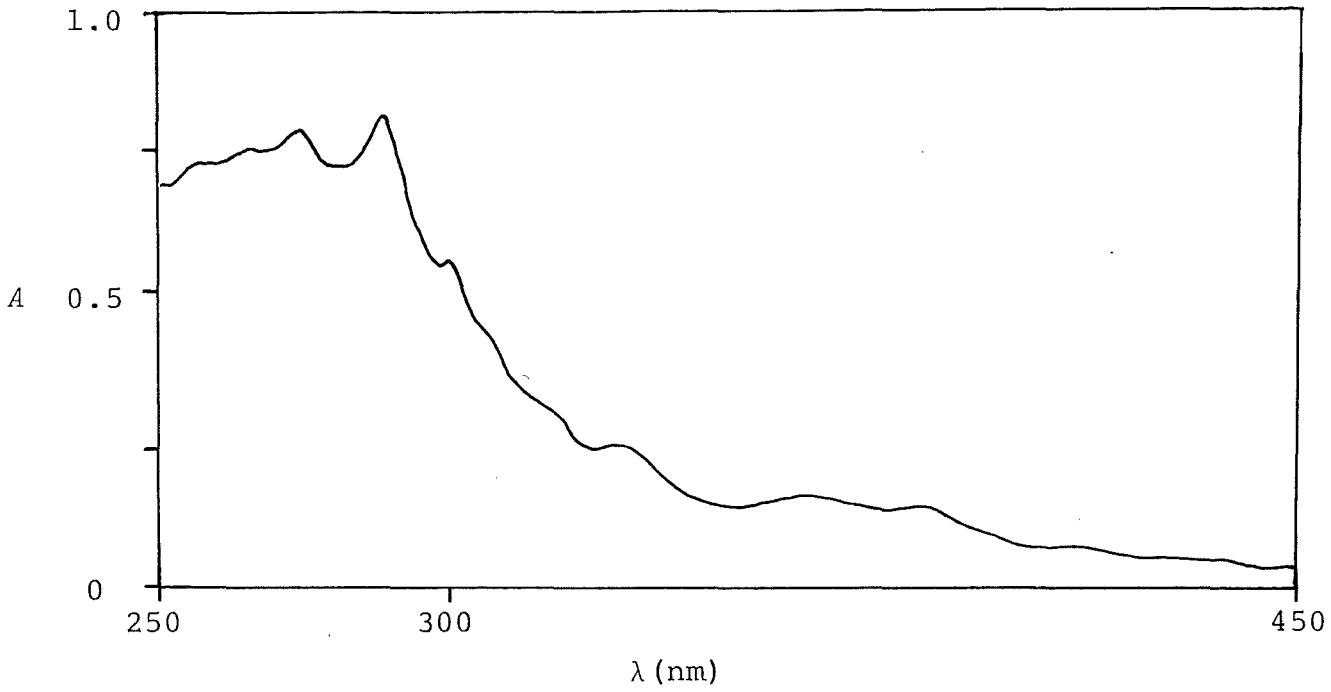


(a) Mud sample

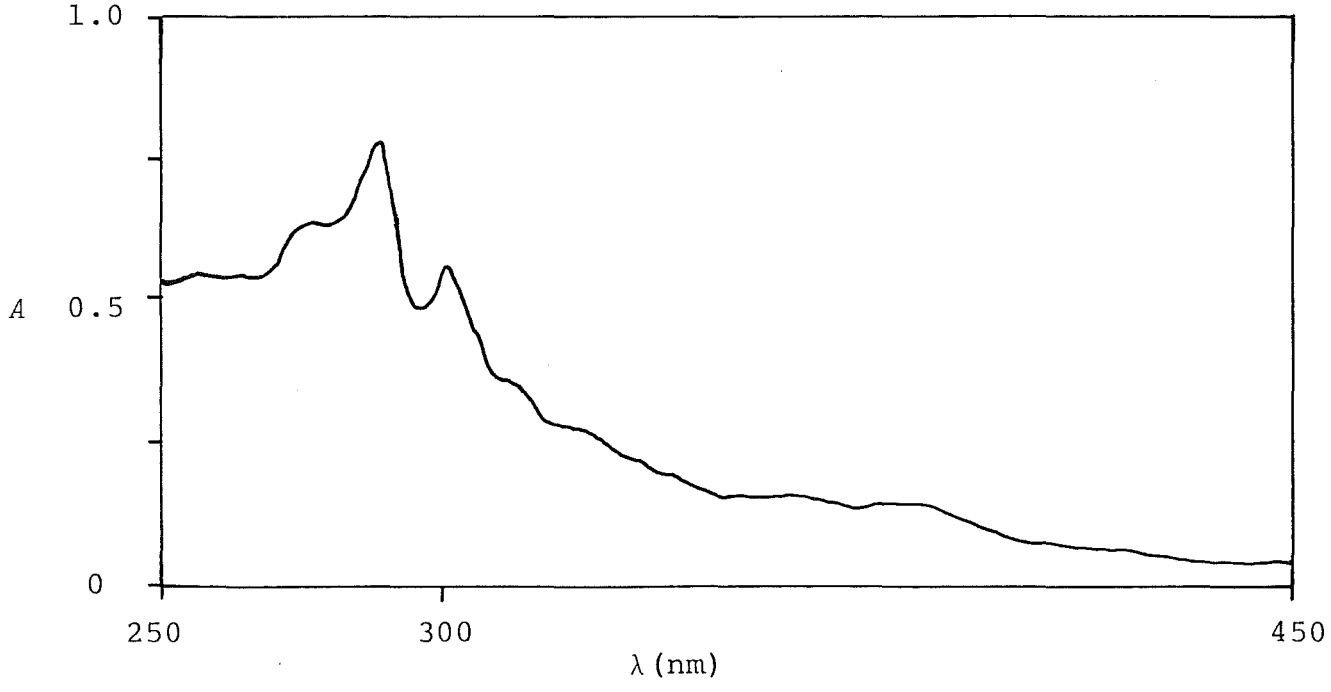


(b) Avonside APM sample

Figure 23. UV spectra of PAH mixtures of samples from various sources.

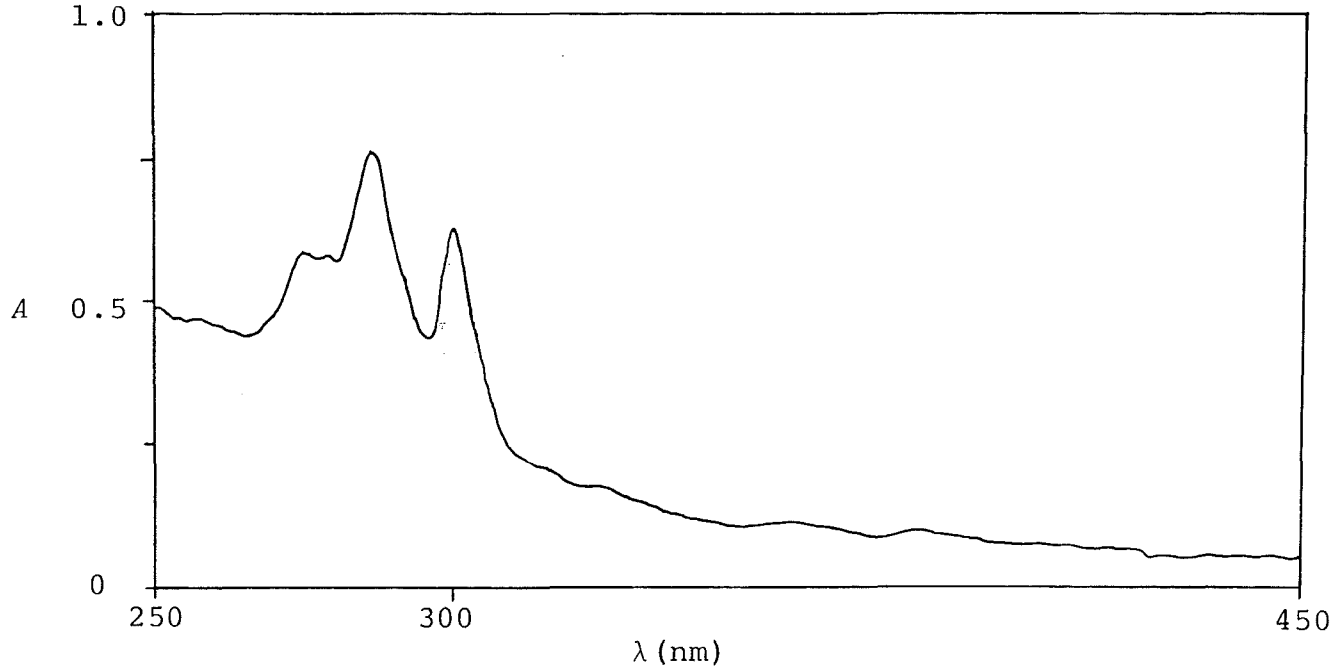


(c) Bealey Avenue APM sample

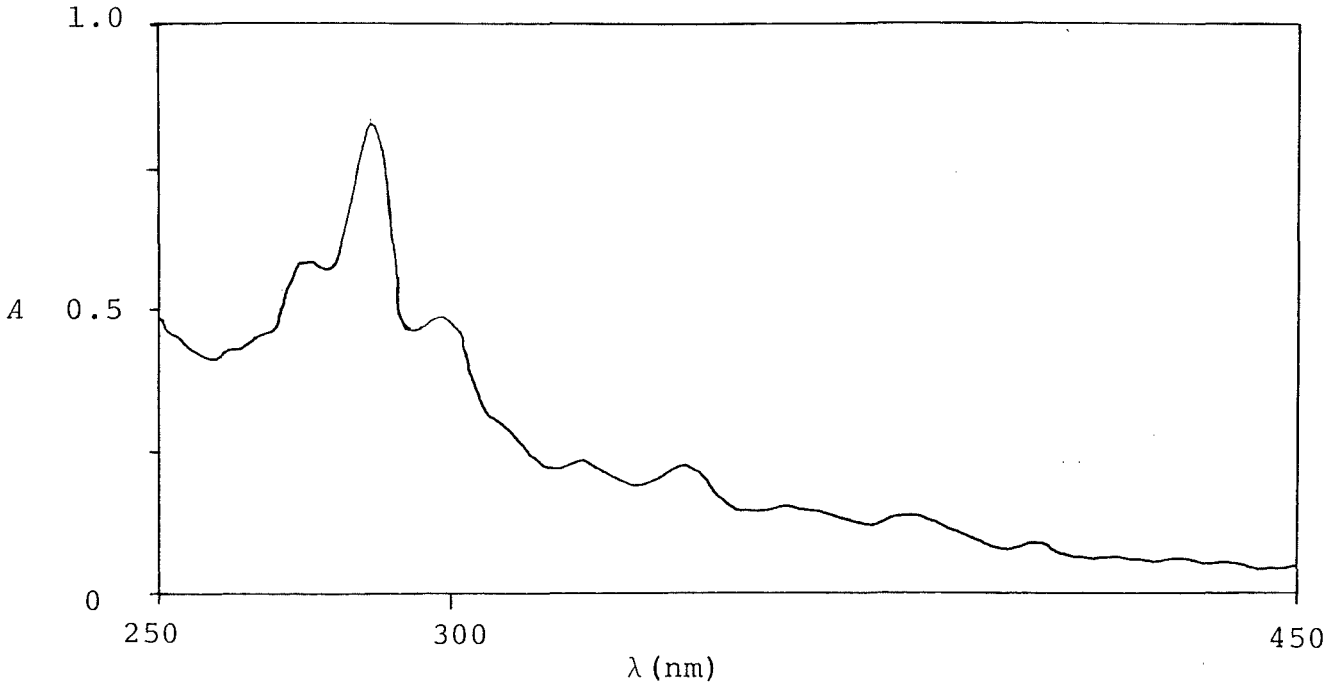


(d) Manchester Street APM sample

Figure 23 (Continued)



(e) Car park building APM sample



(f) Woolston APM sample

Figure 23 (continued)

by the use of parent compound distributions of Bealey Avenue samples (Section 2.4.6). Figure 23(d) and (e) on the other hand all show the characteristics of Figure 22(b), with low intensity absorptions below ca. 285 nm coupled with a major absorption at ca. 300 nm. Again this observation agrees with earlier results about the nature of sources of these samples (that is, traffic-dominated). Obviously, there will be environmental mixing to a certain extent involving all these samples (with the possible exception of car park building samples) and exact resemblances of spectra with those shown in Figure 22 cannot be expected. For example, it is interesting that spectrum (f) in Figure 23 for Woolston is similar to Figure 22(a), in line with the expectation that although Woolston has a mixed domestic-industrial environment its [PAH]/[Pb] ratio would place it in the intermediate-zone, with a greater domestic component (Section 2.3.3). However, although the ca. 285 nm absorption (indicative of domestic pollution, see above) is quite prominent, there is an absence of absorptions below this wavelength; there is also an inflexion at ca. 300 nm, showing that there is perhaps a traffic component in the overall pollution. The placement of this sample in the intermediate-zone is therefore justified by the information provided by the UV spectrum.

As a further extension of this work, an attempt was made to see if minimal clean-up of the samples would give as well-defined (according to source types) spectra as those which had undergone the complete extraction scheme. UV spectra of samples were taken after each of the following

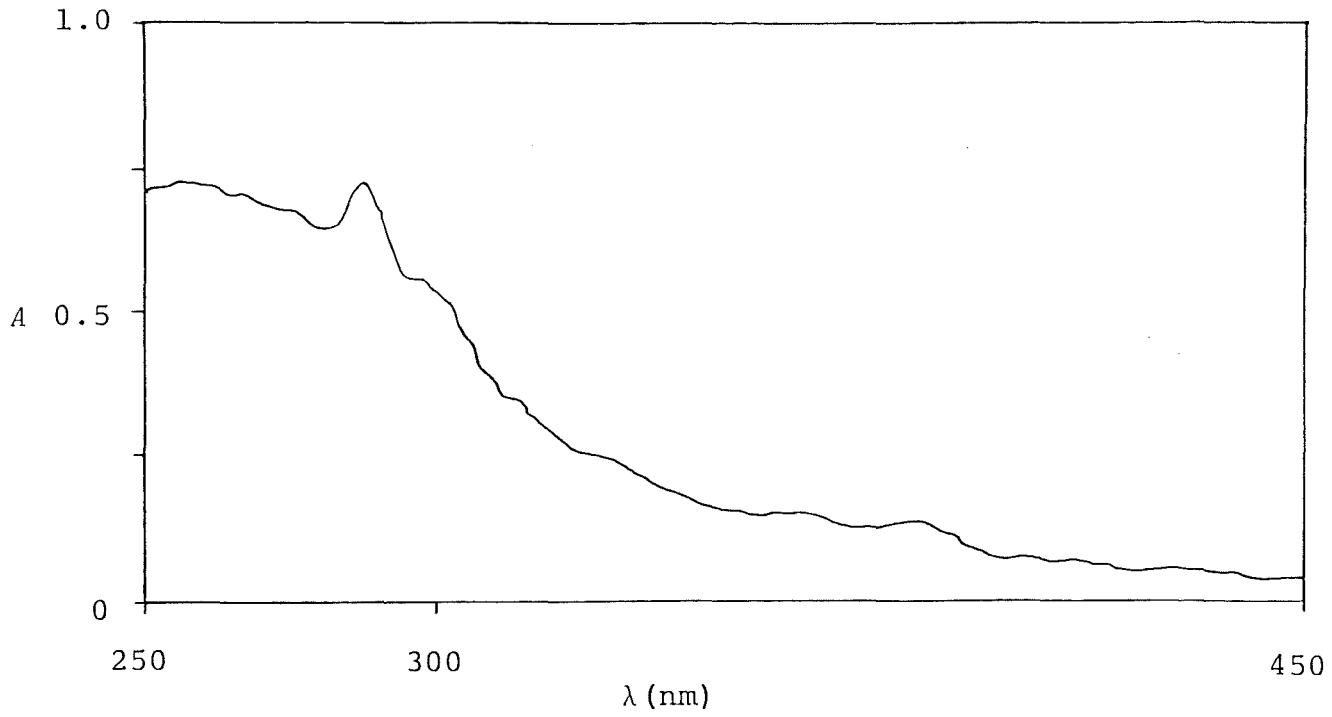


Figure 24. UV spectrum of a PAH mixture of a soot sample taken after silica gel chromatography.

operations: Soxhlet extraction, silica gel, and Sephadex LH-20 chromatography. No distinguishing features were observed in spectra obtained after the Soxhlet extraction; This is not unexpected since many other hydrocarbons are present at this stage. On the other hand, the silica gel eluate showed that, with most of the impurities removed, the spectra were very similar to those taken after the Sephadex LH-20 fractionation. An example is shown in Figure 24 - this spectrum (of a soot sample) is almost identical to that (of a different soot sample) shown in Figure 22(a).

Figure 24 was also found to resemble the spectrum of the same sample obtained after Sephadex LH-20 chromatography, showing that clean-up by silica gel was satisfactory. A further reduction in analysis time is thus possible in this qualitative UV method by dispensing with the Sephadex LH-20 chromatographic step. It is obvious that to obtain spectra of reasonable quality, clean-up by silica gel chromatography is necessary. Sephadex LH-20 chromatography serves to separate the tetra- to heptacyclic PAH from the lower molecular mass components and therefore, by excluding this step, no gross interference should result at the critical absorption wavelengths, at least qualitatively.

The above are only a few examples of many from the various sources considered in this work, that have all been shown to be consistently well correlated with either of the spectra in Figure 22. As a method of determining PAH sources on a preliminary and tentative basis, this qualitative UV technique thus appears to be reasonably reliable as the examples presented here have shown. Concrete conclusions, however, can only be drawn from more rigorous methods, like those involving [BaP]/[BPe] and [PAH]/[Pb] ratios.

2.6 CONCLUSION

This study has shown that the use of [PAH]/[Pb] ratios is a sensitive and effective means of atmospheric PAH source identification. The two main contributors to the PAH load in the Christchurch atmospheric (traffic and domestic soot emissions) can be easily and reliably distinguished by this parameter; in addition, mixed-source emissions can also be differentiated from these two principal PAH sources. The results of this work have also shown that in winter, Christchurch city and suburbs can suffer from high PAH pollution, a problem brought about by climatic and topographical conditions peculiar to the city, as well as the widespread use of coal and coke as fuels in domestic open-fires during this time of year. The similarities of the gas chromatographic profiles of PAH in atmospheric particulates collected from different sites bear testimony to the fact that overall there is a predominant source of these compounds in the Christchurch atmosphere. The resemblance of these profiles with those of domestic soot provides cogent evidence that this source is the domestic open-fire. Localized traffic-dominated emissions contribute to the general levels of airborne PAH but the relative importance of domestic and traffic sources in any sample can only be estimated by the use of [PAH]/[Pb] ratios. Qualitative examination of gas chromatographic profiles of samples from the various APM sampling sites where atmospheric mixing is likely to occur will not distinguish traffic from domestic APM.

It has also been confirmed that the [BaP]/[BPe] ratio can be used as a useful, tentative PAH source indicator, but this relationship lacks the discriminating power and reliability of the[PAH]/[Pb] parameter.

All the evidence available - parent compound distributions and gas chromatographic profiles - indicatesthat the PAH content of the mud in the Avon and Heathcote Rivers and their estuary are representative of the atmospheric PAH load and therefore largely derived from domestic fire emissions. The many modes of transfer of APM into the aquatic environment allows the accumulation of PAH in the mud. The distribution pattern of PAH in the two rivers shows a gradual increase in the levels of these compounds from the respective sources to a maximum just before the saline stretches of the rivers. Thereafter, there is a marked decrease in PAH levels which continues right up to the entrance of the estuary. The reason for this PAH dilution effect is not known; a similar variation observed for PAH in Chione stutchburyi from the estuary can, however, be explained by the types (marine or terrestrial-derived) of organic matter it feeds on, depending on where in the estuary the specimens are collected.

A preliminary study of the use of ultraviolet (UV) analysis as a fast quantitative method for total [PAH] was undertaken. The results suggest that such a method could well be satisfactory, but that a new sampling programme would need to be carried out to test it. However, this study did show that the UV profile of PAH extracts from various samples can be used as a qualitative guide to the major source of the PAH.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 APPARATUS AND MATERIALS

3.1.1 Polycyclic aromatic hydrocarbons (PAH)

4-, 5-, 6- and 7-ring PAH were provided by Prof. G. Grimmer (Biochemical Institute of Environmental Carcinogens, Hamburg, Federal Republic of Germany) and these were used to prepare standard mixtures in redistilled N,N-dimethylformamide or cyclohexane for evaluation of gas chromatographic and gas chromatography-mass spectrometric performance. A standard solution of benzo[b]chrysene in cyclohexane served as the internal standard for the quantification of PAH in the gas chromatographic analyses.

3.1.2 Solvents

All solvents (Analytical- or Reagent-grade) were redistilled before use to remove possible higher-boiling contaminants. Pre-distillation treatment of the various solvents[82] was as follows: (a) Reagent-grade cyclohexane was extracted with concentrated (98 percent) sulphuric acid, washed with distilled water and dried over calcium chloride. Analytical-grade cyclohexane was redistilled without acid washing; (b) N,N-dimethylformamide was shaken with potassium hydroxide pellets (to remove traces of formic acid) and then dried with calcium oxide; (c) Analytical-grade methanol was dried over calcium hydride before redistillation; and (d) 2-propanol was dehydrated by addition of

calcium oxide. Distillation of all solvents (twice, if necessary) was carried out in glass and the solvents were stored in acid-washed glass jars with aluminium foil-lined screw caps or glass flasks with glass stoppers. Freshly distilled water was stored in the same manner.

Cyclohexane and 2-propanol residues from the rotary evaporator could be recycled for subsequent reuse without risk of contamination. Treatment of these solvents was as described above. In recycling used cyclohexane from the liquid-liquid partitioning operations, several more acid washings than usual were required. For this solvent and also 2-propanol residues from the Sephadex LH-20 chromatography, distillation was not carried out to dryness - the last 75 - 100 mL of solvent were discarded.

3.1.3 Glassware

All glassware, including solvent and sample containers, was initially cleaned by soaking in a chromic acid bath (70 mL saturated sodium dichromate solution and 2 L of concentrated sulphuric acid[82]) for several hours and subsequently rinsed thoroughly several times with hot water before being drained and oven-dried. Alconox detergent (Alconox Inc., New York) was found to be satisfactory for cleaning where the use of chromic acid was inconvenient (due to size and quantity of glassware). Glasswool (used as plugs in silica gel columns) was soaked in chromic acid, thoroughly rinsed with water and dried, then silanized (25 mL dimethyldichlorosilane in 500 mL toluene), and

finally extracted with cyclohexane in a Soxhlet apparatus for 8 h.

3.1.4 Column chromatography with silica gel

Chromatography was performed on a 10 mm i.d. x 200 mm glass column with a ca. 100-mL reservoir. The column was packed with silica gel (100-200 μm; Woelm Pharma, Federal Republic of Germany) (4.5 g) in cyclohexane giving a gel bed height of 120 mm. The silica gel was deactivated as follows: distilled water (15 mL) was pipetted into a clean, dry 500-mL round-bottomed flask and swirled around to evenly wet the surface. Silica gel (85 g) was then added to the flask which was stoppered and shaken vigorously until no solid lumps were observed. The flask was left standing for 2 h before use to allow an even distribution of water throughout the silica gel.

3.1.5 Exclusion chromatography with Sephadex LH-20

A slurry of Sephadex LH-20 (25-100 μm; Pharmacia, Sweden) (10 g) in 2-propanol was prepared and poured into a glass column (30 mm i.d. x 100 mm) having a frit insert (in place of a glasswool plug), a Teflon tap with a ca. 100-mL reservoir. Gel bed height was ca. 54 mm.

3.1.6 Filters and thimbles

Glassfibre filters (37-mm diameter; Type A, Gelman, Michigan, USA and Type B, Whatman, England) for airborne particulate matter (APM) sampling and thimbles (glassfibre:

Carl Schleicher & Schüll, Dassel, Federal Republic of Germany; cellulose: Whatman, England) for Soxhlet extractions were pre-extracted (8 h) with Analytical-grade acetone, as were the cellulose backing pads (Gelman) used as filter supports in the field monitors (filter holders) during sampling. The filters and thimbles were dried at 200°C for 3 h. High-volume glassfibre filters (254 mm x 203 mm; Type A, Gelman) were pre-fired at 400°C for 1 h before use. Such pre-treatment of all filters, thimbles and backing pads was necessary to ensure the removal of organic contaminants present in these materials[170] which might lead to interferences in PAH determinations.

3.2 COLLECTION OF SAMPLES

3.2.1 APM from city and suburban atmospheres

(a) General sampling procedure. Field monitors (filter holders) (Gelman) were used to hold the pre-extracted 37-mm diameter backing pads and filters for APM sampling. Two such filter units were used for a particular sampling period (ca. 24 h); these were connected (Tygon tubing) via a glass "Y"-shaped adaptor to a pump (Figure 24) which exhausted the air flow into a gas meter. The adaptor-pump-meter connections were of polyethylene tubing. The volume of air drawn through the filter system was determined from the gas meter which had earlier been calibrated against standardized meters (at flow rates of 1.5 - 6.0 m^3/h) prior to use, and which was accurate to within $\pm$ 1 percent

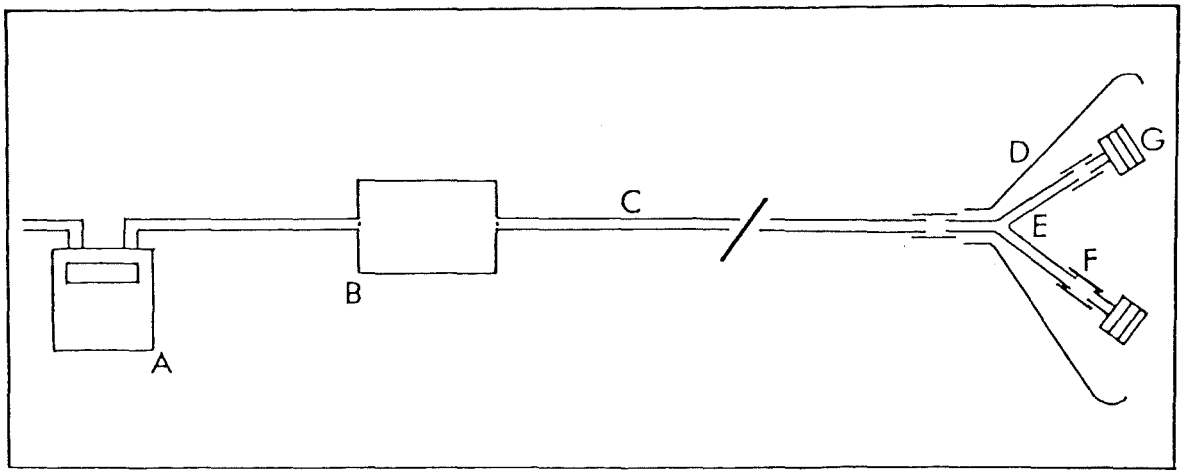


Figure 24 Schematic diagram of the arrangement of the APM sampling equipment. A - gas meter; B - pump; C - polyethylene tubing; D - protective funnel; E - "Y"-adaptor; F - Tygon tubing and G - filter monitor.

in gas volume measurements. For high-volume sampling using the 254 mm x 203 mm filters, a pump unit with an incorporated filter holder and wire-mesh support (for the filter) was used (see below).

(b) Pumping equipment. To collect sufficient APM over a sampling period for PAH determination, a pumping system with a high flow rate was required. Conventional vacuum pumps were found to be unsatisfactory - the higher throughput of air at low vacuum resulted in oil loss and smoke emission. Both oil-less diaphragm and positive displacement rotary oil pumps, however, proved suitable for continuous sampling.

Three pumping systems were used for the 37-mm filters:

(i) Edwards positive displacement rotary oil pump (rated

at 4.9 m^3/h; actual flow rate 4 - 5 m^3/h depending on filter loading); (ii) Thomas 727CD diaphragm pump (6.1 m^3/h; 3.9 - 4.0 m^3/h); and (iii) Two Dynavac 907 CD/107 CD diaphragm pumps (linked in parallel) (2.0 and 1.0 m^3/h respectively; 2.15 - 2.20 m^3/h when linked). The high-volume sampling unit (Gelman) consisted of a two-speed hurricane pump and a filter holder. This pump was used for collecting APM over short periods (up to 2 h). The lower of the two speed settings (ca. 120 m^3/h) was used to avoid overheating the unit which was enclosed in a sound-absorbing box to reduce the noise level when it was in operation.

(c) Filter (37-mm diameter) system. Filters which had been stored in a desiccator over 24 h and weighed, were fitted along with backing pads to the 3-piece clear styrene field monitors. The outer inlet casing of each monitor was removed during sampling to permit the even distribution of APM on the filter. After sampling, the loaded filter was equilibrated for another 24 h in a desiccator and reweighed to determine the quantity of APM collected. Filters were kept in polyethylene bags in cold, dark conditions until ready for Soxhlet extraction.

A single filter unit was initially used for sampling. However, this proved unsatisfactory because the small filter surface area led to a marked pressure drop across it and this resulted in a reduction in flow rate. A better arrangement was to have two monitors linked to a "Y"-shaped adaptor whose stem was connected to the pump. Whatman 37-mm filters

were used before 16th August, 1979, Gelman filters after this date. Treatment of 254 mm x 203 mm filters immediately before and after sampling was the same as that described for 37-mm diameter filters.

(d) Sampling sites. Most of the samples collected for analysis were obtained over 24-h periods (ending at 9 a.m. on the date specified in the Tables in Section 2.3) at four sites used regularly by the New Zealand Department of Health, Air Pollution Monitoring Unit and approved by the World Health Organization as official monitoring sites. These sites were located at Wooston, Bealey Avenue, Manchester Street and Avonside (see Figure 2, Section 2.1.6). Details of local sampling sites and dates of collection are as follows:

(i) Avonside. The sampling site was located 30 m east of England Street approximately 0.25 km from Linwood Avenue. The sampling unit was placed 3.5 m above ground level. Sampling was carried out over the period 5th - 29th July and 17th August - 15th September, 1979.

High-volume samples were also collected from this site. The sampler was situated at a height of 3 m, and samples were taken over 40-min periods within an hour between 8 a.m. and 6 a.m. on 17th August, 1979. During each sampling period, the air flow rate on the sampler flow gauge was recorded at 5-min intervals. Since the drop in flow rate over a period was found to be negligible, the volume of air sampled was calculated simply by multiplying the average air flow rate by the sampling duration.

(ii) Bealey Avenue. The location was an inner city area at the Department of Health, Air Pollution Section, 50 m west of Manchester Street between Salisbury Street and Bealey Avenue. The sampler was placed 2.5 m above the ground. The sampling period was 3rd - 27th July, 1979.

(iii) Manchester Street. The site was in the inner city 2 m east of Manchester Street close to the Manchester Street - Worcester Street intersection. The sampling unit was placed at a height of 2.5 m. Sampling was carried out over the periods 25th July - 24th August and 3rd - 13th September and 5th - 12th December, 1979. High-volume sampling was also carried out at this site.

(iv) Woolston. The sampling site was at the Industrial Health Clinic located in a triangle bounded by Garlands Road and King Edward Terrace. The sampling unit was located 2.5 m above the ground, and samples were collected from 24th August - 13th September, 1979. See Figure 15 for the location of the Woolston industrial region.

3.2.2 APM from city public car park buildings

Three multi-storeyed city car park buildings (CPB) were sampled. Lichfield Street and Oxford Terrace CPB each provided three samples all collected on different days. From Manchester Street CPB, two of the three samples were collected on the same day. Locations of the CPB are shown in Figure 2 (Section 2.1.6).

(a) General sampling procedure. 254 mm x 203 mm filters were used with the hurricane pump for these sites. The sampling

unit was placed ca. 0.75 m off the ground in all locations. Pre- and post-sampling weighing procedures and storage of filters were as previously described (Section 3.2.1c).

(b) Sampling sites

(i) Lichfield Street CPB. The actual sampling site was next to the entrance-exit lane, an area where wind currents were comparatively slight. Samples were collected on 25th, 27th November and 2nd December, 1981 between approx. 2.45 p.m. - 4.30 p.m.

(ii) Oxford Terrace CPB. The site was well into the building in a sheltered location on Level Three. Sampling dates were 7th, 9th and 11th December, 1981 between approx. 2.30 p.m. - 4.30 p.m.

(iii) Manchester Street CPB. The sampling unit was placed next to the exit lane near the toll-operator's booth on Level Two. The area was normally fanned by winds blowing into the building through its open sides. Samples were taken on 15th December (two samples) and 17th December, 1981 from approx. 2.30 p.m. - 4.00 p.m. for the first of the 15th December and the 17th December samples, and approx. 4.00 p.m. - 4.30 p.m. for the second sample of 15th December.

3.2.3 River and estuarine mud

(a) General sampling procedure, storage and clean-up. Mud samples were collected into clean glass jars with aluminium foil-lined screw caps, and stored under cold, dark conditions. Only mud from the surface of the stream bottom was collected.

For drying, the mud was placed in a covered crystallizing dish and left at ambient temperature in a clean area away from light. The dried mass was then pulverized using a mortar and pestle and passed through an 80-mesh sieve. The fines, if not used immediately, were wrapped in aluminium foil for storage until required for analysis.

(b) Sampling sites. Figures 15 and 16 (Section 2.4) show the locations along the Avon and Heathcote Rivers and on the estuary from which mud samples were collected. The river samples were obtained near the bank at low tide; unsubmerged surface mud of depth 0-3 cm was sampled, except along the upper reaches of both rivers where the mud was usually under water. The estuary samples from Sites C1 - C3 were collected at the same time as the bivalve, Chione stutchburyi, specimens, also during low tide (see below). Mud only was collected from Site H.

(i) Avon River. There were two possible sources of this river, both in the same general area (suburb of Avonhead). One was dry (for several kilometres downstream); the other, a spring in the garden of a private house (No. 74, Norton's Road) was sampled. The other sampling sites were:

(2) Okeover Stream, University of Canterbury; between Engineering Road the the Physics Department building.

(3) Straven Road bridge (near Te Kura Street); ca. 1 m upstream of the bridge (north side of the river).

(4) Harper Avenue; Little Hagley, between the ends of Cheltenham and Exeter Streets (south side).

(5) Antigua Street bridge; at the boatsheds, ca. 15 m downstream of the bridge (north side).

(6) Fitzgerald Avenue bridge; ca. 15 m upstream of the bridge (north side).

(7) Gloucester Street North (Dallington) bridge; under the bridge (south side).

(8) Owles Terrace; approx. at the end of Collingwood Street (north side).

(ii) Heathcote River. Of the tributaries arising from the three possible sources of this river, two had industrial and farm wastes discharged into them at or near their origins (these two subsequently join to form a single stream which links up with the main river). The third tributary whose source (as located on a map of this area) was in open farmland, was clear, clean and flowing freely, and the site chosen to represent the "source" was ca. 5 m before the confluence of this tributary and the stream mentioned above (near the motorway bridge). The other sampling sites were:

(B) Spreydon Domain; ca. 30 m downstream of the footbridge (north side of the river).

(C) Cracroft Bridge (Princess Margaret Hospital); under the bridge (south side).

(D) Waltham Road bridge; under the bridge (south side).

(E) Radley Street bridge; under the bridge (south side).

(F) Tunnel Road bridge; ca. 10 m upstream of the bridge (north side).

(G) Ferrymead Bridge; under the bridge (north side).

(H) Estuary; ca. 100 m east of Linwood Avenue - Humphrey's Drive junction.

3.2.4 Bivalves (*Chione Stutchburyi*)

(a) Storage and clean-up. *Chione* specimens, which were collected at low tide, were washed free of mud after being collected, and shucked as soon as possible. The soft tissue, the entirety of which was retained, was kept frozen in glass jars until ready for homogenization and then freeze-drying. The freeze-dried material was kept in the dark until required.

(b) Sampling sites. Three sites on the Avon-Heathcote estuary were selected for *Chione* collection (Figure 16, Section 2.4). Site C1 was on the discharge channel of the oxidation ponds of the Bromley Sewage Treatment Works. The second site C2 was at the southern part of the estuary (ca. 50 m off Beachville Road), and Site C3 was ca. 100 m west of the Brighton sand spit (Plover Street end). Samples from Site C1 were generally covered by several cm of mud and were smaller in size than those collected from the other two sites. Specimens from Sites C2 and C3 were taken from the mud surface. Dates of sampling were 4th April, 1981 (C1), 10th April (C2) and 23rd April (C3).

3.2.5 Domestic open-fire soot

Soot samples were taken from private houses in suburban Christchurch. A variety of materials (coal, coke, garden wood, wood from demolished buildings and pine wood) had been

used as fuels in the fireplaces, all but two of which were of the conventional open-fire type. These two were a chip heater and a "pot-belly" stove. Three samples were provided by the New Zealand Department of Health in Auckland.

General sampling procedure. The samples were taken from the tops of the fireplace chimneys and stored in glass jars. When required for analysis, each sample was sieved through an 80-mesh strainer (after pulverization by mortar and pestle, if necessary). The fines were collected for analysis.

The three Auckland soot samples were obtained by drawing particulate matter from the open-fire through cellulose thimbles.

3.2.6 Automobile (petrol-engined) exhaust emissions

Initially a simplified version of the system described by Grimmer, et al.,[171] was used for collecting exhaust emissions. The exhaust outlet of an automobile was held in place at one end of a horizontal glass cylinder (8 cm i.d. x 1.6 m) which served as the cooling tube for the hot exhaust gases. The filter was introduced at the other end of the cooling tube and placed ca. 0.9 m away from the exhaust pipe. Particulate matter was then collected in the usual way (Section 3.2.1). This system, however, proved unsatisfactory because the temperature within the cooling tube rose well above the maximum recommended temperature limit (66°C) for the filter monitor, causing it to deform. (Grimmer, et al.[171] used metal filter holders and therefore

did not encounter this problem.) Subsequently, a more satisfactory arrangement consisting of a sampling chamber fed from the cooling tube was devised. This chamber not only enabled the filter monitors to be used safely but also avoided the high possibility of degradation of PAH on the filter at excessive sampling temperatures.[115]

The sampling chamber (ca. 2.5 m x 73 cm x 69 cm) was constructed of wood (frame) and clear polyethylene sheets (walls) within a well-ventilated car-port. The ceiling of the car-port formed the chamber while a wooden board served as the base. Since the chamber was not designed to be perfectly airtight, it was not necessary to have any device (flaps, for example) to release the excess pressure during sampling.

(a) Sampling procedure. The exhaust emission was directed into the cooling tube which was connected to a flexible tubing (50 cm x 3 m) discharging into the chamber at a height of ca. 0.3 m. Two filter units connected in the usual way (Section 3.2.1) were introduced into the chamber (ca. 1 m off the base) through a slit in the polyethylene wall for the sampling. A third filter unit connected to a second pump was also used; this sample was for the lead determination. Duration of sampling was ca. 15 min. No problems with high temperatures were encountered - the highest temperature (inside the chamber) recorded was 29°C on one occasion. The chamber was purged between successive sampling by means of a vacuum cleaner.

Filter handling immediately before and after sampling was as previously described.

(b) Pumping equipment. The paired filter units were connected to the Edwards positive displacement rotary oil pump used for APM sampling while a Metrovac rotary vacuum pump (AEI, England) was used for the other filter unit.

3.3 ANALYTICAL METHODOLOGY - POLYCYCLIC AROMATIC HYDROCARBONS

The procedure for the extraction, isolation and quantification of PAH from environmental samples in this work was adapted from that of Grimmer and Böhnke[83] (Figure 25). This method and various versions of it have previously been used for a variety of samples.[47,88,93,98,172]

3.3.1 Extraction of organics

(a) Particulate matter (from air and automobile exhausts), river mud and domestic soot samples. All the organics including PAH were extracted from these samples using a Soxhlet apparatus. Particulate matter-entrained filters, river and estuarine mud (15 - 20 g, dry weight) and domestic soot (0.3 - 1.5 g) were placed in glassfibre or cellulose thimbles for the extraction with cyclohexane (80 - 120 mL) for at least 8 h. The internal standard, benzo[b]chrysene was added before the extraction was commenced. The entire Soxhlet apparatus was wrapped in aluminium foil to prevent the access of light. The extracts were usually a clear yellow colour although those samples containing low concentrations of organics gave almost colourless solutions. River and estuarine mud extracts also emitted an odour reminiscent of decaying organic matter.

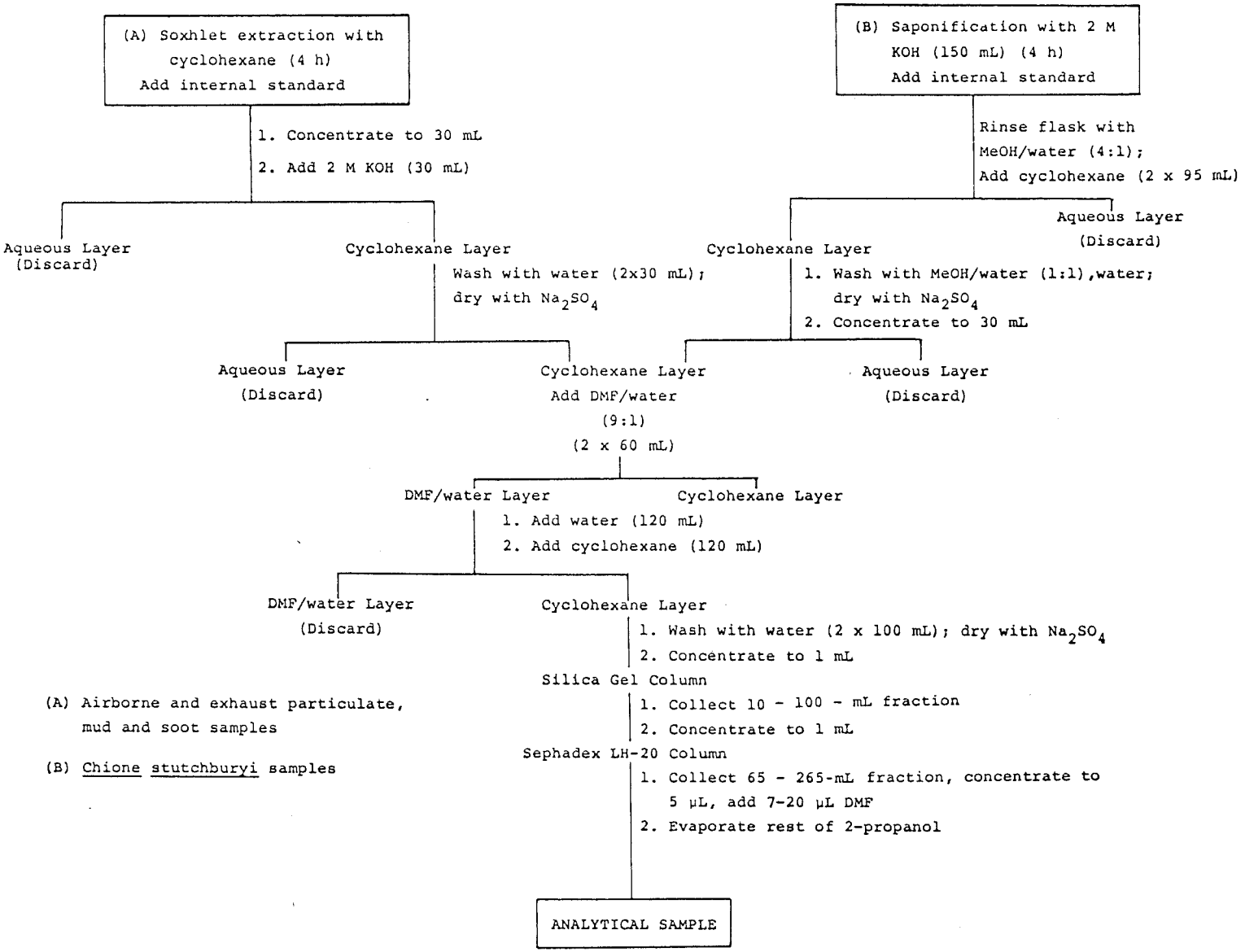


Figure 25. Scheme for extracting PAH from environmental samples.

After the Soxhlet extraction the cyclohexane extract was concentrated down to ca. 30 mL under reduced pressure using a rotary evaporator and transferred to a 100-mL separating funnel to which was also added 2 M potassium hydroxide in methanol-water (4:1, v/v)(30 mL). The mixture was shaken vigorously and the layers allowed to separate. The lower aqueous layer was discarded and the cyclohexane phase washed twice with distilled water (30 mL) to remove traces of base. After separating the two layers, the cyclohexane extract was dried with Analytical-grade sodium sulphate, and transferred to a 250-mL separating funnel. N,N-dimethylformamide (DMF)-water (9:1, v/v)(2 x 60 mL) was then added to extract the PAH from the cyclohexane, by agitating the mixture and allowing the layers to separate. The lower DMF-water layers were combined in a 500-mL separating funnel where back-extraction into cyclohexane was carried out by the addition of water (120 mL) and cyclohexane (120 mL). The DMF-water layer was discarded and the cyclohexane washed with water (2 x 100 mL). After drying with sodium sulphate, the cyclohexane solution was transferred to a 250-mL round-bottomed flask and evaporated under reduced pressure to ca. 1 mL.

Auckland coal soot samples were collected on thimbles which were therefore extracted as they were. An unused thimble was used as a blank in a preliminary evaluation for possible interferences in the PAH determination. The rest of the extraction procedure was as above.

(b) Chione samples. Freeze-dried material (20 - 30 g) was initially saponified by refluxing for 4 h with 2 M potassium hydroxide (in methanol-water, 4:1)(150 mL) in a 500-mL round-bottomed flask. While still warm, the resulting solution was transferred to a 500-mL separating funnel; the flask was rinsed with methanol-water (4:1)(2 x 25 mL) and the washings added to the original solution. The combined methanol-water mixture was then extracted with cyclohexane (95 mL). Gentle rocking of the separating funnel, rather than vigorous shaking, appeared to give well-separated phases without the formation of emulsions at the interface (provided complete hydrolysis had been achieved). The lower aqueous layer (which included the solid residues) was drained into a second 500-mL separating funnel and extracted again with cyclohexane (95 mL); the aqueous layer was then discarded. The cyclohexane extract in the first separating funnel was then washed with methanol-water (1:1)(50 mL) which was subsequently drained into the second separating funnel to wash the second portion of cyclohexane. After this methanol-water mixture had been discarded, the two cyclohexane phases were washed with water (2 x 50 mL) in a similar way. The cyclohexane phases were then combined, dried with sodium sulphate and evaporated under reduced pressure to ca. 30 mL. Extraction with DMF-water and subsequent back-extraction into cyclohexane was then carried out as before, as well as the concentration of the cyclohexane to ca. 1 mL.

3.3.2 Sample pre-factionation

The 1-mL concentrate from the liquid-liquid partition step was placed on top of the silica gel column; the round-bottomed flask was rinsed twice with cyclohexane (ca. 1 mL) and the washings added to the top of the column, which was then eluted with the same solvent. The first 10-mL fraction of eluate was discarded and the next 90-mL fraction collected into a pre-rinsed (with cyclohexane) 250-mL round-bottomed flask and evaporated under reduced pressure to ca. 1 mL. The silica gel column served to remove impurities from the sample, and a yellow band of these could usually be observed at the head of the gel bed. The silica gel was discarded after use.

To further fractionate the PAH of interest (4-, 5-, 6- and 7-ring compounds) from others of lower molecular masses and also to remove other impurities (mainly higher-boiling hydrocarbons), the Sephadex LH-20 column was used. 2-Propanol (ca.1 mL) was added to the cyclohexane residue from the silica gel chromatographic step and the resulting concentrate was placed on the Sephadex LH-20 column. The original flask was rinsed out with 2-propanol (2 x ca. 0.5 mL) and the washings added to the column. The latter was then eluted with 2-propanol. The (0 - 65)-mL fraction, containing hydrocarbons (0 - 38 mL) and low molecular mass PAH (38 - 65 mL) was discarded while the (65 - 265)-mL fraction (or more until after the green tint in the column had disappeared) containing the PAH of interest was collected and concentrated under reduced pressure to 10 - 20 mL and then transferred to

a 50-mL flask which had been drawn to a taper at the bottom. Further concentration of the eluate under reduced pressure was carried out until ca. 1 mL of solvent (within the taper) remained. At this stage, a stream of dry nitrogen passing through a stainless steel column packed with Porapak Q (Waters, Massachusetts, USA) (to remove traces of hydrocarbons from the nitrogen) was used to evaporate the 2-propanol, with several washings of the sides of the flask with solvent. Just before the last trace of solvent was completely removed, DMF (7 - 20 μL, depending on the sample) from a microlitre syringe was added to the flask. This concentrate was kept under cold, dark conditions (usually for not more than a few hours) until required for analysis. The Sephadex LH-20 column was prepared for use for another sample by eluting it with 80 - 100 mL of 2-propanol.

Generally, an entire extraction was performed under subdued light conditions to prevent possible photodegradation of the PAH.

3.3.3 Qualitative and quantitative analysis of PAH

(a) Gas chromatography. The separation of individual PAH components was achieved by gas chromatography (GC). A Hewlett-Packard 5710A gas chromatograph with a flame ionization detector was modified for the installation of a capillary column injection system (Chromalytic Technology, Australia) having a splitter/splitless injection mode. A glass capillary (support-coated open tubular, SCOT) column coated with OV-101 stationary phase (0.5 mm i.d. x 25 m; Chromalytic

Technology, Australia or 0.5 mm i.d. x 55 m; SGE, Australia) was used for analysis. For PAH quantification, gas chromatographic peak areas were measured by cutting and weighing (in quintuplicate), manual measurement and electronic integration (Hewlett-Packard 3390A Integrator).

Typical gas chromatographic conditions for an analysis were:

Detector temperature:	250°C
Injection port temperature:	300°C
Column temperature:	260°C (isothermal) or programmed from 245° to 270°C (at 4°/min for 1 min, 8°/min thereafter)
Helium carrier gas flow:	5-6 mL/min
Make-up gas (helium) flow:	30 - 35 mL/min
Septum purge flow:	1 mL/min

A brief description of the splitter/splitless injection system is helpful at this stage. In the splitter mode, a glass-lined vaporiser tube (1.8 mm i.d.) into which the sample is injected is used. Sample splitting occurs within this tube, the split ratio being adjusted by a needle valve which leads to atmosphere. For splitless injections, the vaporiser tube is replaced by a different tube which has a smaller i.d. glass-lined insert within it. The needle valve is open in this case (1 turn, as recommended by the manufacturer) giving an effluent flow rate of 2-3 mL/min to atmosphere.

Both splitter and splitless injection modes were used in this work. A split ratio of between 10 and 20:1 was

typical for split injections. If it was surmised (from the very pale yellow colour) that the PAH concentration in a sample was very low, the splitless mode was used instead.

Cold column trapping[173,174]

A concentration technique known as cold-column trapping was used occasionally for qualitative gas chromatographic analysis. The sample was injected when the column was at ambient temperature, allowing the solvent to vent through while the PAH components were concentrated at the head of the column. Several injections could be made this way before temperature-programming was effected. The peaks that appear were usually sharp with a minimum of broadening due to the absence of solvent interference.

(b) Gas chromatography-mass spectrometry. Combined gas chromatography-mass spectrometry was used to identify those PAH components not characterised by GC, and also to confirm the identities of those which were. The system used was a Hewlett-Packard 5982A gas chromatograph-mass spectrometer. The gas chromatograph was the same one used for the flame ionization detection analyses. The 0.5 mm i.d. x 25 m OV-101 capillary column was used to separate the PAH mixtures and introduce the components into the source for mass spectral analysis. The column was interfaced with the mass spectrometer via the chemical ionization transfer line (although the source was set at the electron impact mode). Gas chromatographic conditions were generally similar to those used for

the flame ionization detection runs (with temperature-programming). Peaks eluting from the gas chromatograph were scanned across a mass range of 90 - 350 amu at a rate of 100 amu/s with the mass spectrometer being operated at 70 eV ionizing energy. Other relevant mass spectrometric conditions were:

Auxillary temperature	300°C
Source pressure	3×10^{-5} Torr
Ion source manifold temperature	270°C
Detector gain	HI/1-3
Make-up gas (helium) flow	30 mL/min.

3.4 ANALYTICAL METHODOLOGY - LEAD

3.4.1 Sample treatment[140]

All glassware used for sample work-up was cleaned by soaking in concentrated (14 M) nitric acid for several hours; then thoroughly rinsed with distilled water and oven-dried.

(a) Airborne particulate matter. This description applies to APM collected from city and suburban atmospheres, public car park buildings and automobile exhausts.

A core taken from each sample (see below) was digested (1 h) in 4:1 concentrated nitric acid - concentrated hydrochloric acid (both Analytical-grade; Univar, Sydney, Australia) (5 mL) and distilled water (5 mL) in a 50-mL beaker. Following this, the solution was filtered through an acid-washed glassfibre filter paper (GF/A; Whatman) into a 10-mL volumetric flask. The volume was then made up to

10 mL with distilled water. Where it was necessary to use more than 10 mL to quantitatively transfer the sample solution, a 20- or 25-mL volumetric flask was used, with the volume made up accordingly with distilled water. An unused filter was digested and treated in a similar manner to act as blank. The solutions were than analysed directly by flame atomic absorption spectrophotometry, along with a series of lead standard solutions for calibration.

(i) Coring of samples. A quarter segment from one of the two 37-mm diameter filters obtained in daily sampling, or from the individual (Metrovac pump) filter collected in the automobile exhaust sampling programme was used for analysis. In preliminary tests, it was ascertained that such a segment represented 1/4 of the total particulate matter on the filter to within $\pm$ 1% of the expected value. For the high-volume filters, a rectangular core representing 10 percent of the filter area was taken for the analysis.

(ii) Distribution of lead on filters. Three 1/4 segments taken from both samples for one daily sampling period were analysed separately, and were found to have identical quantities of lead, indicating uniform radial distribution of lead on the filters, as might be expected from the uniform distribution of particulate matter established in (i) above.

(b) River and estuarine mud. The procedure for mud (fines, 1-2 g dry weight) was the same as that described for APM, except that the digestion mixture was 2 M nitric acid (15 mL) which was prepared by diluting 14 M nitric acid (71 mL) with distilled water (429 mL), and the final solutions

for analysis were made up to 20 or 25 mL. The blank consisted of the digesting mixture which was treated in the same way.

(c) Domestic open-fire soot and Chione. Open-fire soot (0.2 - 1 g) and Chione tissue (2.5 - 3.5 g dry weight) were treated in the same manner as mud samples, including the blank. The only difficulty was that, perhaps because the samples were finely-divided, filtration (into 10-mL flasks for soot samples, 20- or 25-mL flasks for Chione samples) did not remove the solid material satisfactorily. However, by using two layers of Whatman No. 40 filter paper, a better separation was achieved. As mentioned previously, the Auckland soot samples were collected on thimbles. These were analysed by carefully cutting the thimbles into strips so that they could be accommodated in the beakers for the acid digestion. An unused thimble was used as the blank sample.

3.4.2 Lead standard solutions

A stock standard solution of lead (1000 ppm) was prepared by dissolving lead nitrate (Analytical-grade; BDH, England) (0.7993 g) in distilled water (500 mL). Appropriate standards of varying concentrations were prepared from this stock solution for the calibration curve for each analysis. These calibration standards were freshly prepared as required and then discarded after use.

3.4.3 Flame Atomic Absorption Spectrophotometry (AAS)

Analysis for lead was carried out by flame AAS using a Varian Techtron AA5 with an oxidizing acetylene-air flame. The wavelength selected was 217 nm. To determine the level of lead in the sample solutions, a linear calibration curve produced from the concurrent analysis of a series of lead standard solutions was used. Corrections were made relative to the background lead levels determined in the blank solutions.

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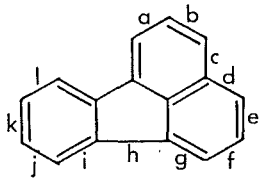
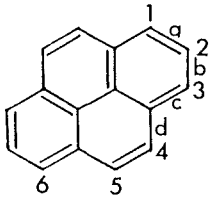
APPENDIX A

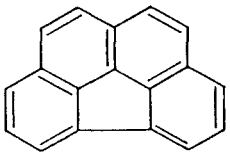
Structures, nomenclature and carcinogenic activities of some Polycyclic Aromatic Hydrocarbons



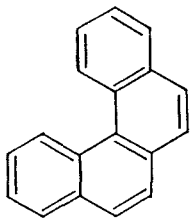
Fluoranthene (inactive[95])



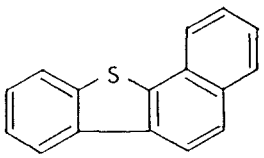
Pyrene (inactive[32,95])



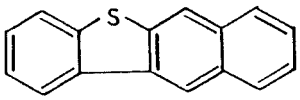
Benzo[ghi]fluoranthene (inactive[175])



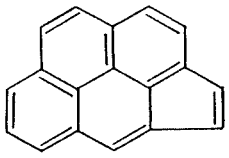
Benzo[c]phenanthrene (moderate[32])



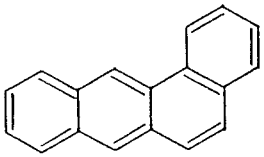
Benzo[b]naphtho[2,1-d]thiophene (?)



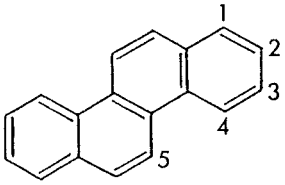
Benzo[b]naphtho[2,3-d]thiophene (?)



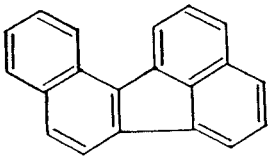
Cyclopenta[cd]pyrene (active[176,177])



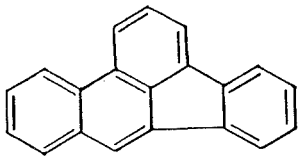
Benz[a]anthracene (disputed[32,95])



Chrysene (disputed[32,95])

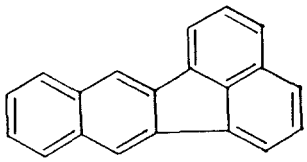


Benzo[j]fluoranthene (moderate[32,95])



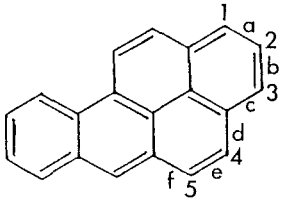
Benzo[b]fluoranthene
(benz[e]acephenanthrylene)

(weakly active[95])



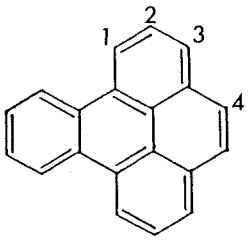
Benzo[k]fluoranthene

(disputed[32,95])



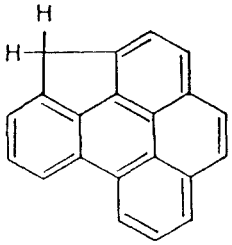
Benzo[a]pyrene

(highly active[32,95])



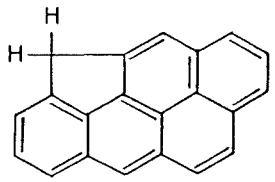
Benzo[e]pyrene

(inactive[32]/
weak[95])

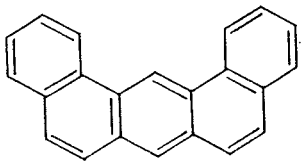


Methylenebenzo[e]pyrene

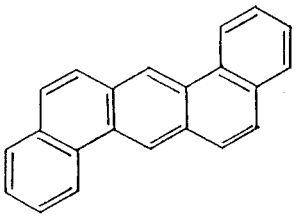
(active[177])



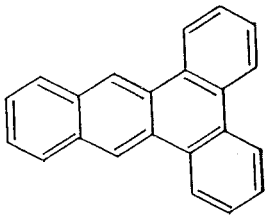
Methylenebenzo[a]pyrene (active[177])



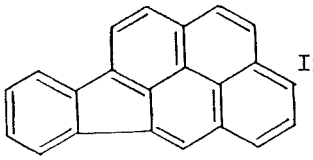
Dibenz[a,j]anthracene (moderate[32])



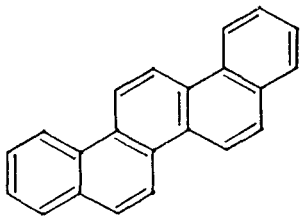
Dibenz[a,h]anthracene (moderate, more active then [a,j]isomer[32])



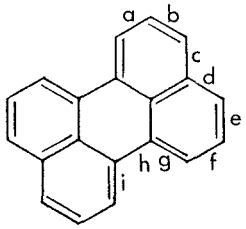
Dibenz[a,c]anthracene (disputed[32,39])



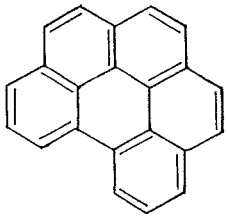
Indeno[1,2,3-cd]pyrene (weakly active[95])



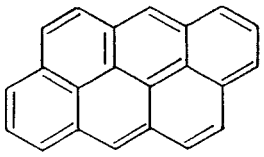
Picene (inactive[32])



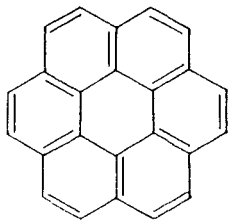
Perylene (inactive[32])



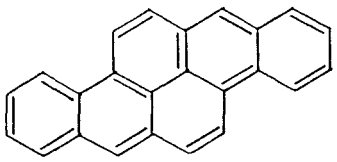
Benzo[ghi]perylene (inactive[95]/moderate[32])



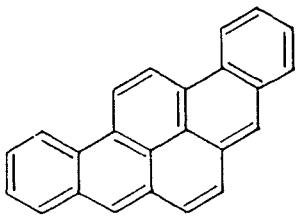
Anthanthrene
(dibenzo[cd,jk]pyrene) (inactive[32,95])



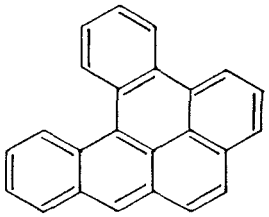
Coronene (inactive[95])



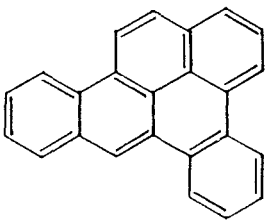
Dibenzo[a,h]pyrene (moderate[95]/ high activity[32])



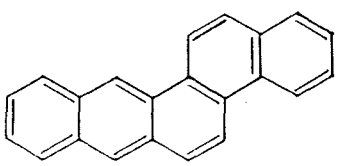
Dibenzo[a,i]pyrene (moderate[95]/ high activity[32])



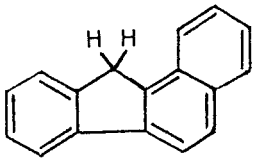
Dibenzo[a,l]pyrene (moderate[95]/ high activity[32])



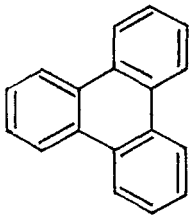
Dibenzo[a,e]pyrene (high activity[32])



Benzo[b]chrysene (inactive[32])



Benzo[a]fluorene (inactive[175])



Triphenylene (inactive[32])

APPENDIX B

(i) An example of a single-variable analysis.

To calculate the F values (variance ratios) of the $\log_{10}$([PAH/[Pb]) values for Manchester Street (MS) and Avonside (AV) sites, the method used is shown below.

Single-variable analysis

		MS(n_1 = 12)	Av(n_2 = 7)
$\log_{10}$(PAH]/[Pb])		0.4973	1.2234
		0.7931	1.2479
		1.0107	1.1319
		0.8618	1.1811
		0.5895	1.1383
		0.6386	1.1602
		0.6820	1.2898
		0.9741	
		0.6021	
		0.5217	
		0.9198	
		0.8138	
Total,	Σx	8.9045	8.3726
Mean,	$\bar{x}$	0.7420($\bar{x}_1$)	1.1961($\bar{x}_2$)
Sum of squares,	Σx^2	6.9528	10.0356
	$\frac{(\Sigma x)^2}{n}$	6.6075	10.0143
	$\Sigma x^2 - \frac{(\Sigma x)^2}{n}$	0.3453	0.0213

Sum of squares within group, xx = 0.3453 + 0.0213

= 0.3666

Pooled estimate of variance, $s_x^2 = xx/n_1 + n_2 - 2 = 0.02156$

(Difference between sample means)$^2 = d^2 = (\bar{x}_1 - \bar{x}_2)^2 = 0.20621$

$$\text{Variance of ratio, } F = \frac{n_1 n_2}{n_1+n_2} \cdot \frac{d^2}{s_x^2} = \underline{42.29}$$

Degrees of freedom: $\nu_1 = 1$ (one variable), $\nu_2 = n_1+n_2 - 2 = 17$

F_{tab}(at the 1 percent significance level) = 8.40

Thus, $\log_{10}$([PAH]/[Pb]) values for Manchester Street and Avonside sites are significantly different from each other. Variance ratios for Manchester Street/Bealey Avenue and Avonside/Bealey Avenue $\log_{10}$([PAH]/[Pb]) values (or any other variable) are calculated in the same way.

(ii) An example of a multivariate (two-variable) analysis

Two variables associated with one site are analysed jointly with those of another site. In this example, the variables used are [BaP] and [BPe] and the sites considered are Manchester Street and Avonside.

(ii) Two-variable analysis

	Manchester Street		Avonside		Group Sizes
	[BaP] (x_1)	[BPe] (y_1)	[BaP] (x_2)	[BPe] (y_2)	
	8	14	71	33	
	15	16	19	11	n_1=12 n_2=8
	18	28	57	37	n_1+n_2 = 20 (=N)
	32	24	23	18	
	10	11	29	22	
	13	19	36	21	
	11	12	70	28	
	38	33	66	37	
	11	14			Differences between group means
	12	17			
	20	23			
	17	25			
Total	205	236	371	207	$d_1=\bar{x}_1-\bar{x}_2$ = -29.30
Mean	17.08	19.67	46.38	25.88	$d_2=\bar{y}_1-\bar{y}_2$ = - 6.21
	Sum of squares		Sum of squares		Pooled within groups
(area)A	4425	5166	20573	5981	(xx)=923+3368 = 4291
(area)C / ssq	3502 / 923	4641 / 525	17205 / 3368	5356 / 625	(yy)=525+625 = 1150
	Sum of products		Sum of products		(xy)=578+1271 = 1849
(area)A	4610		10871		
(area)C	4032		9600		
spt	578		1271		

$$\text{Estimate of covariance} = \frac{(xy)}{(n_1+n_2-2)} = \frac{1849}{18} = 102.7$$

$$s_1^2 = s_x^2 = \frac{(xx)}{N-2} = \frac{4291}{18} = 238.4 \text{ and } s_1^2 = s_y^2 = \frac{(yy)}{N-2} = 63.9$$

$$(xx)a_1 + (xy)a_2 = (N-2)d_1$$
$$(xy)a_1 + (yy)a_2 = (N-2)d_2$$

$$4291a_1 + 1849a_2 = 18 \times (-29.30) = -527.4$$
$$1849a_1 + 1150a_2 = 18 \times (-6.21) = -111.8$$

Solving for a_1 and a_2: $a_1 = -0.26381711$, $a_2 = 0.32695465$

Squared distance between the two groups, $D^2 = a_1d_1 + a_2d_2 = 5.699$

Hotelling's $T^2 = \frac{n_1n_2}{n_1+n_2} D^2 = \frac{12x8}{20} (5.699) = 27.3552$

$p = 2$ (number of variables considered)

$$\therefore \quad F = \frac{N-p-1}{(N-2)p} T^2 = \frac{20-2-1}{18x2} (27.3552) = 12.918$$

$\nu_1 = p = 2$, $\nu_2 = N - p - 1 = 17$: $F_{tab} = 6.11$ at the 1 percent level.

Table XVIII. F values (Variance Ratios) Calculated from Single- (a) and Two-variable (b) Analyses of PAH and Pb Data given in Tables II-IV. MS: Manchester Street; AV: Avonside and BA: Bealey Avenue

(a)

	MS/AV	MS/BA	AV/BA
F_{tab} @ 1 percent sig. level	8.29	8.40	9.07
$\log_{10}$([PAH]/[Pb])	44.03	15.92	9.31
[PAH]/[Pb]	27.12	17.91	5.30
[BAP]/[BPe]	40.96	21.98	3.33
$\log_{10}$([BaP]/[BPe])	44.16	21.60	3.60

F_{tab} @ 1 percent sig. level	8.40	8.40	9.33
$\log_{10}$([PAH]/[Pb])*	42.29	17.56	11.30

*Errant Avonside value (Section 2.3.1) not included

(b)

F_{tab} @ 1 percent sig. level	6.11	6.25	6.93
$\log_{10}$([PAH]/[Pb]) and [BaP]/[BPe]	29.50	12.86	4.50
[PAH]/[Pb] and [BaP]/[BPe]	23.72	13.66	2.93
$\log_{10}$([PAH]/[Pb]) and $\log_{10}$([BaP]/[BPe])	29.51	12.55	4.49
[BaP] and [BPe]	12.92	8.07	1.81

Table XIX. F values calculated (Single-variable analysis) using Log_{10}([PAH]/[Pb]) data by considering Manchester Street (MS), Avonside (AV), Car Park Building (CPB), Automobile Exhaust (AE) and Domestic Soot (DS) Samples

	AE/DS	AE/CPB	CPB/DS	MS/CPB	AV/DS
F_{cal}	53.90	1.56	49.99	34.30	10.78
(F_{tab} @ 1 percent level)	(8.10)	(8.29)	(8.29)	(8.18)	(8.53)

ACKNOWLEDGEMENTS

I am particularly grateful to Dr G.J. Wright and Dr W.H. Swallow (Chemistry Division, Department of Scientific and Industrial Research, Christchurch) for their encouragement and help in this study. The help of Dr J.R. Cretney (Christchurch Polytechnic) and Mr R.K. Panckhurst (Technical Staff, Chemistry Department) in the sampling programme is very much appreciated. Dr Cretney also carried out the lead determinations of some of the airborne particulate matter samples. I also thank Dr L.K. Pannell (Chemistry Division, DSIR) and Dr J.A. Robb (Christchurch Drainage Board) for very informative discussions.

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